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Solvent Influence on Selectivity in α -Pinene Oxide Isomerization Using MoO₃-Modified Zeolite BETA

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Abstract: Natural source turpentine is an available source of α -pinene oxide. This compound's value is especially given by the possibility of producing important compounds campholenic aldehyde and *trans*-carveol. In this work, we would like to present the usage of MoO₃-modified zeolite BETA in α -pinene oxide isomerization concerning campholenic aldehyde and *trans*-carveol formation using a wide range of solvents. Catalyst calcination temperature also influenced the reaction course (selectivity to desired compounds and reaction rate). MoO₃-zeolite BETA was prepared by the wet impregnation method and characterized by different techniques. The use of polar aprotic solvents had the most positive effect on the reaction course. Solvent basicity and polarity considerably influenced the reaction rate and selectivity to particular products. The combination of high basicity and the high polarity was the most suitable for the studied reaction from the reaction rate point of view. Selectivity to campholenic aldehyde and *trans*-carveol was the most influenced by solvent basicity. Higher solvent basicity caused the preferential formation of *trans*-carveol, influence on selectivity to campholenic aldehyde formation was the opposite. The described catalyst may be used for α -pinene oxide rearrangement to both desired products dependently on the used solvent. Molybdenum offers an exciting alternative for previously described modifications of zeolites for this reaction.

Keywords: α -Pinene oxide; campholenic aldehyde; *trans*-carveol; isomerization; MoO₃-zeolite BETA

1. Introduction

α -Pinene oxide is an important compound, which does not occur in nature itself. Still, simple oxidation of α -pinene—a natural compound abundant present in renewable source turpentine (obtained from biomass processing) [1]—leads to α -pinene oxide. The most valued compounds, which can be obtained from this compound isomerization, are campholenic aldehyde and *trans*-carveol. Campholenic aldehyde, which itself possesses by a gently woody smell, can be further used to synthesize fragrances with sandalwood scent (e.g., sandalore, Figure 1), *trans*-carveol can be part of fragrances bearing caraway and spearmint scent.

Figure 1. Structure of *trans*-carveol (a), campholenic aldehyde (b) and sandalore (c).

Several biological activities (antimicrobial, anticancer [2,3]) accompany these substances. Abrushov synthesis [4,5] serves as a process for campholenic aldehyde preparation using homogeneous catalyst zinc (II) bromide biotransformation of *d*-limonene led to *trans*-carveol [6]. Usage of heterogeneous catalysts in this reaction can offer environmental aspects (not handling corrosive mixtures, the possibility of catalyst reuse). Many researchers gave attention to the study of various heterogeneous catalysts in α -pinene oxide isomerization in recent years. Many catalysts based on (alumo)silicates was already tested, among them iron-modified zeolites or mesoporous sieves, providing > 60% selectivity of campholenic aldehyde formation [7–13]. Preferential formation of *trans*-carveol [14,15] was described using titanium modified materials [16–18], Sn-SiO₂ with 70% selectivity of *trans*-carveol formation [19], methyl(trioxo)rhenium-Al₂O₃ providing total conversion in a single minute [20], and 83% selectivity of *trans*-carveol formation, Ce-MCM-41 [21] or tungsten modified SiO₂ [22,23]. Some literary data describe the influence of solvent on selectivity in α -pinene oxide rearrangement toward particular products. Above all, using iron- or titanium-modified materials [7,9,14,16,17]—overall results showed that usage of basic polar solvents favored in most cases the formation of *trans*-carveol and using of nonpolar solvents campholenic aldehyde formation. On the other hand, selectivity which product occurs from α -pinene oxide rearrangement is given by a specific combination of temperature, catalyst, and solvent type (e.g., modified clays—high selectivity of fencholenic aldehyde formation was reported [24]).

Molybdenum modified materials are active acid catalysts (because of material Lewis acidity enhancement due MoO₃ content [25,26]) and may serve as catalysts in alkane isomerization [27–31]. Usage of molybdenum-based catalyst in α -pinene oxide is also reported [32]. Based on these facts, we decided to prepare several types of molybdenum modified zeolites BETA and test a large number of different solvents concerning campholenic aldehyde and *trans*-carveol selectivity.

2. Results and Discussion

2.1. Material Preparation and Characterization

Several types of Mo-modified materials were prepared by wet impregnation method of BETA38 zeolite. The wet impregnation method is commonly used for zeolite modification and was performed using two temperatures based on the literature data: 60 °C [10,14] (for materials 20Mo450, 20Mo500, 20Mo550, 20Mo600) and RT (20Mo450RT) [25,26]. The effect of calcination temperature on the material properties and catalytic activity was also tested—calcination temperatures 450, 500, 550 and 600 °C (used calcination temperature is contained in materials name—e.g., 20Mo550 was calcined at 550 °C).

To determine the optimal calcination temperature, the temperature programmed heating was applied to non-calcined material precursor obtained after the wet impregnation method (Figure 2). TCD (thermal conductivity detector) signal helped us to determine the temperature at which all molybdate decomposed to MoO₃. This temperature was about 450 °C. We applied four calcination temperatures starting from 450 °C on material precursor in connection with this finding.

Figure 2. TCD (thermal conductivity detector) signal from temperature programmed heating of noncalcined sample.

X-ray fluorescence (XRF) analysis of samples confirmed that all samples contained appropriate Mo amount corresponding to the desired (20 wt.%) content of molybdenum in catalyst (Table 1).

Table 1. X-ray fluorescence (XRF) analysis results.

Material	MoO ₃ (%)	Mo (%) calculated	SiO ₂ (%)	Al ₂ O ₃ (%)	Others (%)
20Mo450	32.8	21.6	63.7	3.4	0.1
20Mo450RT	36.0	23.7	60.8	3.1	0.1
20Mo500	32.0	21.1	64.7	3.2	0.1
20Mo550	33.2	21.9	63.5	3.2	0.1
20Mo600	33.9	22.3	62.9	3.1	0.1

X-ray diffraction (Figure 3) confirmed the crystal structure of zeolite BETA38—characteristic bands for aluminosilicate (7.8, 12.8, 14.6, 21.4, 22.5, 25.4, 25.6, 27.3, 28.9, 29.6, 43.6 2Theta°) were present [33]. Materials modified with MoO₃ contained aforementioned characteristic bands (with the exception of 20Mo600) for aluminosilicate. This fact revealed that inserting MoO₃ did not destroy the zeolite structure. Bands characteristic for MoO₃ (12.8, 23.3, 27.3, 33.2, 33.8, 38.9, 39.5, 45.8, 46.3, 49.3, 52.8, 55.2, 56.4, 58.8, 64.5, 69.6, 72.8, 76.5, 78.8 2Theta°) [34] were also present. The presence of intensive bands for MoO₃ corresponded to the fact that the sample contained a large amount of MoO₃, which was not homogeneously dispersed [35]. Materials 20Mo550 and 20Mo600 were partially amorphous, which was especially visible by the absence of a band at 7.8 2Theta° and a decrease of some other bands' intensity characteristic for aluminosilicate.

Table 2 summarizes the results of the textural analyses of the catalysts. All samples of catalysts show adsorption isotherms of type Ib and IVa (Figure 4, IUPAC classification), so samples consist of micropores and mesopores with classical type hysteresis loop H1 (IUPAC classification), which corresponds to a narrow range of uniform mesopores. The exception is the catalyst 20Mo600, which contains almost only mesopores (the adsorption isotherm is only type IVa). All samples of prepared materials contain a mixture of micropores and mesopores, but the samples differ in the ratio of micropores and mesopores.

Figure 3. X-Ray diffractograms of nonmodified BETA38 and molybdenum modified materials (° aluminosilicate bands, * Mo bands).

Table 2. Textural characteristic of prepared materials and unmodified BETA38 zeolite.

Material	S_{BET} m ² /g	$S_{\text{t-plot}}$ m ² /g	Total Pore Volume cm ³ /g	t -Plot Micropore Volume cm ³ /g	Ratio of Micropores (%)
BETA38	539.62	136.15	0.341	0.210	61.6
20Mo450	272.81	58.70	0.181	0.110	60.8
20Mo500	239.46	53.98	0.171	0.096	56.1
20Mo550	154.33	43.47	0.139	0.057	41.0
20Mo600	16.50	12.43	0.057	0.002	3.5
20Mo450RT	269.30	61.61	0.184	0.107	58.1

Figure 4. Adsorption isotherms of nonmodified BETA38 and molybdenum modified materials.

The total pore volume of pores less than 40 nm diameter at $p/p^\circ = 0.95$ (V_{total}) of modified materials was found in the range from 0.184 cm³/g to 0.057 cm³/g, but the micropore volume (t-plot method) was in the range from 0.110 cm³/g to 0.002 cm³/g.

We observed sealing of pores connected with a decrease of specific surface area and decrease of micropore ratio with higher calcination temperature. Influence of temperature used during impregnation—room temperature or 60 °C did not influence textural characteristics of material (similar values in all measured parameters).

Nitrogen physisorption showed a significant decrease of catalyst specific surface area with using higher calcination temperature. This fact can also be visible from particle size distribution (Figure 5); in case of higher calcination temperatures, the increase of particle size is visible. Particles with larger size, present in 20Mo550, and 20Mo600 materials can be attributed to agglomerate formation using higher calcination temperatures. Non-modified BETA38 showed rather uniform distribution and can be classified as a monodisperse system, whereas modified materials are rather polydisperse systems.

Figure 5. Particle size distribution of nonmodified BETA38 and molybdenum modified materials.

In all cases, after modification of material with MoO₃, particle sizes $D_{v(50)}$ and $D_{v(90)}$ increased compared to non-modified BETA38 material (Table 3). Materials prepared by wet impregnation at 60 °C (20Mo450) and at room temperature (20Mo450RT) possess very similar $D_{v(50)}$ and $D_{v(90)}$ —1.64 and 1.94, and 35.2 and 44.2, respectively. A slight increase of value $D_{v(90)}$ was observed when calcination temperature 500 °C was used (20Mo500). These results also corresponded to specific surface area results, where these materials had very similar characteristics. Another situation was observed using higher calcination temperatures—a significant increase in $D_{v(50)}$ and $D_{v(90)}$ values was observed—again, this is in accordance with physisorption measurement results, where a significant decrease of specific surface area was observed after calcining samples at 550 and 600 °C.

Table 3. Particle characteristic of prepared materials.

Material	Span Value	Particle Size (μm)		
		$D_{v(10)}$	$D_{v(50)}$	$D_{v(90)}$
BETA38	1.6	0.39	0.71	1.6
20Mo450	22.2	0.43	1.64	35.2
20Mo450RT	22.5	0.44	1.94	44.2
20Mo500	47.9	0.46	1.74	55.0
20Mo550	81.9	0.50	4.74	389.0
20Mo600	43.8	0.58	16.20	710.0

Morphology of materials surface was monitored using scanning electron microscopy (Figure 6). Elemental mapping confirmed the homogeneous distribution of molybdenum on the material surface, and no difference was observed between the materials. SEM images of materials BETA38, 20Mo450 and 20Mo600 are provided in supplementary material (Figures S1, S2 and S3).

Figure 6. SEM image of 20Mo450 (a) and 20Mo600 (b) material with elemental maps of Si and Mo.

2.2. Catalytic Testing

α -Pinene oxide isomerization can provide different products—among them, the most mentioned and valued are campholenic aldehyde and *trans*-carveol. Using our reaction system—molybdenum modified zeolite BETA38, the most abundant products were (Figure 7)—campholenic aldehyde (CA), *trans*-carveol (TCV), and *p*-methadien-2-ol (PMD). In some cases, *p*-cymene and *sobreol* were present in the reaction mixture (this diol occurs predominantly in the presence of water in a reaction system). The isomer of campholenic aldehyde—fencholenic aldehyde was in our reaction system present only in small amounts (<5%), which was not surprising because its origination literature reported only using other types of catalyst (e.g., acid-treated clays [24]).

Figure 7. Reaction scheme: campholenic aldehyde (a), fencholenic aldehyde (b), *trans*-carveol (c), *p*-methadien-2-ol (d), *p*-cymene (e), and *sobreol* (f).

In the beginning, the activity of BETA38 (used as solid support of our catalysts) and activity of molybdenum-based catalysts prepared by different methods was compared (Figure 8).

Figure 8. Reaction result using zeolite BETA38 and materials modified with 20 wt.% of molybdenum prepared by different ways (1.25 g APO, 6 mL of toluene, 0.125 g of catalyst, 70 °C, 3 h).

The positive influence of molybdenum loading is visible—using unmodified zeolite BETA38 resulted in only low APO conversion (34%, 3 h) compared to Mo-modified materials (77–100%, 3 h). No significant difference was observed based on the preparation of materials either by wet impregnation at room temperature or by wet impregnation at 60 °C (both materials calcined at 450 °C). The selectivity of PMD formation differed only slightly (12% for RT and 14% for 60 °C), and this difference was only in the range of measurement error. On the other hand, the temperature of calcination after impregnation showed to be a crucial parameter—it significantly influenced APO conversion. Using the calcination temperatures 450 and 500 °C resulted in the same conversion of APO – 100% after 3 h. However, a further increase of calcination temperature led to APO conversion decrease (83% for 550 °C and 77% for 600 °C). A calcination temperature 550 °C caused a slight increase in CA selectivity. A significant loss of material surface area connected with higher calcination temperature was definitely the reason for the loss of material activity. We have chosen 20Mo450 material to test the influence of solvent type on reaction course (Table 4). Reaction course of reactions using different solvents are depicted in supplementary material (Figures S4–S6).

Table 4. Reaction results using different solvents (1.25 g APO, 6 mL of solvent, 0.125 g of catalyst 20Mo450, 70 °C, 3 h) [36–40].

Solvent	Solvent Type	Donor Number (kJ/mol)	Dielectric Constant (Relative Permittivity)	Initial Reaction Rate (mmol/gcat.min)	APO Conversion at 3 h (%)	CA Selectivity at 3 h (%)	TCA Selectivity at 3 h (%)	PMD Selectivity at 3 h (%)
cyclohexane	nonpolar	0	2.02	2.40	99	34.6	17.4	13.9
toluene	nonpolar	0.1	2.38	5.43	100	34.2	14.8	14.0
1,4 dioxane	nonpolar	14.3	2.25	6.63	100	28.7	18.0	11.0
nitromethane	polar aprotic	2.7	35.87	4.68	86	44.9	10.7	12.3
butan-1-ol	polar protic	19.5	17.8	13.11	100	3.2	7.0	1.9
propan-1-ol	polar protic	19.8	21.8	13.11	100	3.3	6.4	2.7
propan-2-ol	polar protic	21.1	17.9	13.11	100	18.2	14.2	5.4
dichlorobenzene	polar aprotic	3	9.93	2.67	100	42.1	13.3	13.1
benzonitrile	polar aprotic	11.9	26	0.71	16	66.5	9.8	0.0
acetonitrile	polar aprotic	14	37.5	0.68	10	62.7	4.9	2.9
ethylacetate	polar aprotic	17.1	6.02	2.67	97	37.1	15.8	13.9
pentan-2-one	polar aprotic	17.1	18.2	11.32	100	35.1	15.5	12.0
butan-2-one	polar aprotic	17.4	18.5	11.95	100	30.8	10.4	9.1
cyclohexanone	polar aprotic	18	18.2	8.34	100	37.4	15.0	16.6
tetrahydrofuran	polar aprotic	20	7.58	6.74	100	31.7	28.9	6.5
cyclohexanol	polar protic	25	15	5.58	100	24.1	21.1	5.1
<i>N,N'</i> -dimethylformamide	polar aprotic	26.6	36.7	1.01	27	26.5	43.8	14.0
<i>N</i> -methylpyrrolidone	polar aprotic	27.3	32.17	0.85	41	26.1	42.9	12.2
<i>N,N'</i> -dimethylacetamide	polar aprotic	27.8	37.8	4.65	44	25.3	45.5	11.5
dimethylsulfoxide	polar aprotic	29.8	46.7	0.97	45	25.3	53.6	12.7
pyridine	polar aprotic	33.1	12.4	0.14	3	55.6	18.5	0.0

It is known that used solvent can significantly influence the reaction course; in our case of APO rearrangement, the selectivity to specific products would be the most important parameter. So far, to the best of our knowledge, widely studied solvent influence was performed using iron-based catalysts (Fe-zeolite, Fe-MCM-41) in APO rearrangement [15,21,41]. A wide number of solvents—nonpolar, polar protic, and polar aprotic—were used and further described using donor number to compare their Lewis basicity and dielectric constant to compare their polarity. Three nonpolar solvents were tested—toluene, cyclohexane, and 1,4-dioxane (Figure 9).

Figure 9. Reaction result using catalyst 20Mo450 and different nonpolar solvents (1.25 g APO, 6 mL of solvent, 0.125 g of catalyst, 70 °C, 3 h).

We obtained similar reaction results using nonpolar solvents comparing APO conversion and selectivity to single compounds (Figure 9). The most significant result can be observed in the initial reaction rate, which was using cyclohexane almost three times slower compared to toluene and 1,4-dioxane. On the other hand, the highest initial reaction rate was observed using 1,4-dioxane. In the case of nonpolar solvents, campholenic aldehyde was the major product, which is in accordance with the results already published in the literature [19,23,41]. As basicity cannot be the main reason (the difference between donor number of toluene and cyclohexane is negligible), other factors have to play an important role.

Usage of polar protic solvents—alcohols—was disadvantageous (Figure 10). Alcohols reacted with APO forming products with higher MW; it is likely that addition on a C-C double bond or oxirane ring-opening occurred. Nitromethane behaved differently probably (Table 4) because either by its different structure or by the fact that both its dielectric constant (35.9 vs. 15–21.8) and its donor number (2.7 vs. 19–25) are far different from dielectric constants and donor numbers of aforementioned alcohols. Using noncyclic alcohol, the total conversion of APO was obtained in the first 5 minutes of reaction.

We tested a large number of polar aprotic solvents following in this reaction (Table 4)—among them, the lowest APO conversions were obtained using pyridine and nitriles (acetonitrile, benzonitrile). In the case of pyridine, this fact was probably caused by its highest Lewis basicity from all studied solvents, which probably caused the blockage of acid sites present on catalyst surface. Pyridine is also known due to its strong adsorption on acid sites. It is the reason why this compound is used for basicity determination by different methods. Low catalytic activity in acetonitrile is in accordance with already published results using similar type of catalyst—Ti-BETA [16] and could be caused by its semi-basic

character together with its high polarity. These both solvents provided low APO conversion (10–16%, 3 h), but high selectivity of CA formation (63–67%). Usage of *N,N'*-dimethylformamide offered only low APO conversion (27%, 3 h), which was surprising, as *N,N'*-dimethylacetamide provided almost twice higher APO conversion.

Figure 10. Reaction result using catalyst 20Mo450 and different polar protic solvents (1.25 g APO, 6 mL of solvent, 0.125 g of catalyst, 70 °C, 3 h).

Polar aprotic solvents, which were able to provide APO conversion > 40% (3 h) and selectivity to sum of CA, TCV, and PMD > 50% (3 h) were chosen to evaluate the influence of dielectric constant and donor number on the reaction course.

The initial reaction rate (Figure 11) was independent on dielectric constant and on donor number, the highest values were obtained using ketones with mediate polarity and basicity from all studied solvents.

Figure 11. Initial reaction rate using different polar aprotic solvents (1.25 g APO, 6 mL of solvent, 0.125 g of catalyst 20Mo450, 70 °C, 3 h).

With the respect to APO conversion dependence on solvent polarity and basicity (Figure 12), the studied solvents were divided into two groups, with exception for nitromethane. Nitromethane did not fit in the studied influence of solvent donor number or dielectric constant on APO conversion. Its unique character compared to other studied aprotic solvents (low Lewis basicity and high polarity) could cause this. Excluding nitromethane, the first solvent group contained mediate polar and basic solvents (dielectric constant 5–20, donor number 3–20), and the second group – high polar and high basic solvents (dielectric constant 32–47, donor number 27–30). High APO conversion (96–100%, 3 h) was observed using the first solvent group. Among the second solvent group, significantly lower APO conversion was observed (41–45%, 3 h), which could probably be caused by the fact that basic solvents caused partial blockage of catalyst acid sites.

Figure 12. APO conversion using different polar aprotic solvents (1.25 g APO, 6 mL of solvent, 0.125 g of catalyst 20Mo450, 70 °C, 3 h), dichlorobenzene (DCB), butan-2-one (BN), cyclohexanone (CYN), *N,N'*-dimethylacetamide (DMA), dimethylsulfoxide (DMSO), ethylacetate (EtOAc), *N*-methylpyrrolidone (NMP), nitromethane (NM), pentan-2-one (PN), tetrahydrofuran (THF).

The solvent basicity significantly influenced the selectivity of CA and TCV (Figure 13), the effect of solvent polarity was not so straightforward. Overall, the selectivity of TCV formation increased with solvent basicity. On the other hand, the selectivity of CA formation decreased with increasing solvent basicity. Solvent basicity influenced CA and TCV formation considerably more than solvent polarity. The influence of solvent basicity on CA and TCV formation was in accordance with previously published results in the case of iron modified zeolite BETA or $H_3PW_{12}O_{40}$ [14,23,41].

We observed similar CA selectivity (3 h) using both nitrobenzene and dichlorobenzene. It was probably caused by the fact, that these solvents possessed very similar Lewis basicity (donor numbers 2.7 and 3).

The selectivity of CA formation (Figure 14a) decreased with APO conversion in the case of dichlorobenzene, ethylacetate, *N*-methylpyrrolidone, and dimethylsulfoxide. In the case of other solvents, it remained the same in the range of measurement error. The selectivity of TCV formation (Figure 14b) was independent on APO conversion (was in the range of measurement error) in the case of most of the solvents except for *N*-methylpyrrolidone and dimethylsulfoxide. In the case of these

two solvents, the selectivity of TCV formation increased significantly with increasing APO conversion. Especially DMSO was the most valuable solvent for the formation of TCV.

Figure 13. Selectivity to CA (black square), TCV (red circle) and PMD (blue triangle) using different polar aprotic solvents (1.25 g APO, 6 mL of solvent, 0.125 g of catalyst 20Mo450, 70 °C, 3 h).

Figure 14. Dependence on campholenic aldehyde (CA, **a**) and *trans*-carveol (TCV, **b**) formation selectivity on APO conversion using different polar aprotic solvents (1.25 g APO, 6 mL of solvent, 0.125 g of catalyst 20Mo450, 70 °C) dichlorobenzene (DCB), butan-2-one (BN), cyclohexanone (CYN), *N,N'*-dimethylacetamide (DMA), dimethylsulfoxide (DMSO), ethylacetate (EtOAc), *N*-methylpyrrolidone (NMP), nitromethane (NM), pentan-2-one (PN), tetrahydrofuran (THF).

Based on literature, we proposed mechanism of two main products formation—CA and TCV (Figure 15).

Figure 15. Proposed mechanism for CA and TCV formation; LAS represents Lewis acid sites of MoO_3 .

Lewis acid site (LAS) activated epoxide ring in APO molecule inducing ring opening and formation of carbenium cation **I**. Cation **I** might rearrange to secondary cyclopentanoic cation **II** and tertiary *p*-menthenic cation **III**. Tertiary cation **III** is more stable than secondary cation. Therefore, the formation of TCV should be thermodynamically controlled and CA formation should be kinetically controlled [19]. In the case of polar solvents, their solvation ability plays a role in cation **I** stabilization, which would lead to the preferential formation of cation **III**. Moreover, in the case of the basic solvents, the proton transfer to cation **III** can be assisted by the solvent, causing the preferential formation of TCV. CA formation from cation **II** by C-C bond cleavage is then preferred in cases when the formation of cation **III** is not favored, i.e., using nonpolar and nonbasic solvents [19].

3. Materials and Methods

Materials were prepared by wet impregnation from zeolite BETA (Si/Al = 38, CP814C, Zeolyst Int., Kansas city, KS, USA) and ammonium heptamolybdate tetrahydrate (Chemapol, Praha, Czech Republic, >99.5%). Two different wet impregnation processes were used: impregnation at room temperature [25,26,42] and at 60 °C [14]. To prepare the material with the desired Mo amount 20 wt.% 6.4 g of molybdate and 10 g of zeolite BETA was used. Different calcination temperatures were used (450–600 °C). We denoted with the names containing calcination temperature and in the case of impregnation performed at room temperature also letters RT (Table 5).

Table 5. Denotation of prepared materials.

Material Denotation	Temperature of Wet Impregnation	Calcination Temperature (°C)
20Mo450RT	room temperature	450
20Mo450		450
20Mo500		500
520Mo550	60 °C	550
20Mo600		600

In a typical reaction procedure, a round bottom flask was filled with solvent (6 ml), α -pinene oxide (1.25 g, Sigma Aldrich, Darmstadt, Germany, 97%), and the mixture was heated to 70 °C. Then catalyst (125 mg, calcined before reaction at 300 °C/air/4 h) was inserted into the reaction mixture, and the suspension was vigorously stirred for the next 3 hours at 70 °C. A wide number of solvents were used: 1,4-dioxane, *N,N'*-dimethylformamide, dimethyl sulfoxide, acetonitrile, cyclohexanone, cyclohexane, tetrahydrofuran, butan-1-ol, propan-1-ol, propan-2-ol, ethylacetate, toluene (all Penta, Praha, Czech Republic, >99.5%), butan-2-one, pyridine, butan-2-ol, (all Lachner, Neratovice, Czech Republic, > 99%), 1,2-dichlorobenzene, benzonitrile, cyclohexanol (all Sigma Aldrich, Darmstadt, Germany, 99%), nitromethane, *N,N'*-dimethylacetamide (both Sigma Aldrich, Darmstadt, Germany, 95%), *N*-methylpyrrolidone (Honeywell, Charlotte, NC, USA, 99%) and pentan-2-one (Aroma Praha, Židovice,

Czech Republic, 95%). The reaction mixtures were analyzed using a gas chromatograph (Varian CP-3800, Palo Alto, CA, USA) equipped with a nonpolar column (DB-5) and FID, conversion (x_{APO}) and selectivity (s) were calculated according to the following equations. Representative chromatogram of reaction mixture is depicted at Figure S7.

$$x_{APO} = 100 - \text{relative concentration}_{APO} \quad (1)$$

$$s_i = \frac{\text{relative concentration}_{APO}}{x_{APO}} \quad (2)$$

Prepared materials were characterized by X-Ray spectroscopy (X-Ray powder diffraction data were collected at room temperature with an X'Pert PRO θ – θ powder diffractometer with parafocusing Bragg–Brentano geometry using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$, $U = 40 \text{ kV}$, $I = 30 \text{ mA}$) and X-ray fluorescence (an ARL 9400 XP sequential WD-XRF spectrometer was used to perform XRF analysis). Temperature programmed heating of non-calcined material was carried out using an AutoChem II Micromeritics Instrument 2920 (Unterschleissheim, Germany). Catalyst sample (0.1 g) was placed in a quartz U-shaped tube and during pretreatment the material was heated to $150 \text{ }^\circ\text{C}$ under argon flow (30 mL/min) and kept under this temperature for 1 h to remove physisorbed water. Afterward, the linear temperature program ($10 \text{ }^\circ\text{C min}^{-1}$) started at a temperature of $150 \text{ }^\circ\text{C}$ and the sample was heated up in argon flow (30 mL/min) to a temperature of $700 \text{ }^\circ\text{C}$. The specific surface area was determined using nitrogen adsorption (3Flex volumetric analyzer, Micromeritics, Unterschleissheim, Germany). The specific surface area of materials was calculated via the BET equation and t -plot method. The particle size distributions of all samples were determined by laser light scattering Malvern Mastersizer 3000 system equipped with Hydro EV wet sampling unit (Malvern Instruments Ltd., Cambridge, UK). The materials were characterized using a wet dispersion method. For each sample, particle size distributions were recorded for at least 5 determinations at an obscuration range of 8 to 14%. The particle size distributions of all materials were determined using demineralized water (conductivity $< 1 \text{ }\mu\text{S}\cdot\text{cm}^{-1}$) with surfactant Triton X-100 (Aldrich, Darmstadt, Germany) as a dispersion medium. The reference refractive index for materials was 1.446. For SEM analysis, materials were applied on carbon adhesive tape and then goldened by 5 nm of gold via Quorum Q150 ES (Quorum Technologies Ltd., Laughton, UK). Scanning was performed by scanning electron microscope TESCAN VEGA 3 LMU (Tescan Brno, Czech Republic) in regime low vacuum (UniVac) at pressure in working chamber 1 Pa, accelerating voltage 20 kV and BSE mode. For elemental analysis EDS analyzer OXFORD Instrument X-max 20 mm^2 with software Aztec (Oxford Instruments, Abingdon, UK) was used.

4. Conclusions

We demonstrated solvent influence on α -pinene oxide (APO) isomerization using molybdenum modified zeolite BETA. The type of used solvent had a significant impact on the reaction course. Nonpolar solvents provided $> 95\%$ APO conversion (3 h), and the major product was campholenic aldehyde. Usage of polar protic solvents was disadvantageous, as they reacted with the substrate preferentially. Among polar aprotic solvents, we observed more trends that are interesting. Basic solvents (dimethylsulfoxide, N,N' -dimethylacetamide, N,N' -dimethylformamide, N -methylpyrrolidone) provided significantly high selectivity of *trans*-carveol formation ($>42\%$, 3 h) but at low APO conversion (27–45, 3 h). Using ketones, total APO conversion was obtained within 3 h of the reaction, with the preferential formation of campholenic aldehyde (30–37% selectivity, 3 h). When using ethylacetate, dichlorobenzene, and nitromethane, high APO conversion ($> 86\%$, 3 h), and preferential formation of campholenic aldehyde (37–45%) were observed. In nitriles, the highest selectivity of CA formation ($\sim 64\%$, 3 h) was obtained. However, APO conversion was very low (10–16%, 3 h). Pyridine showed to be an inappropriate solvent for this reaction. Only 3% APO conversion was present after 3 h. Its highest Lewis basicity from all studied solvents probably caused this fact. We showed that Mo modified zeolite beta is a possible available catalyst for the production

of both campholenic aldehyde and *trans*-carveol. The modification of zeolite beta by molybdenum was advantageous for the reaction course. Moreover, we showed that the calcination temperature and solvent choice are critical parameters in the studied reaction.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/11/1244/s1>, Figure S1: SEM images of BETA38, Figure S2: SEM images of 20Mo450, Figure S3: SEM images of 20Mo600, Figure S4: Reaction course using solvent toluene (catalyst 20Mo450, 70 °C), Figure S5: Reaction course using solvent nitromethane (catalyst 20Mo450, 70 °C), Figure S6: Reaction course using solvent dimethylsulfoxide (catalyst 20Mo450, 70 °C), Figure S7: Representative chromatogram of reaction mixture (solvent toluene).

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