

# Fe-Modified Zeolite BETA as an Active Catalyst for Intramolecular Prins Cyclization of Citronellal

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### Abstract

Prins intramolecular cyclization of citronellal giving desired product isopulegol was performed using different modified zeolites BETA (Si/Al ratio 25, 38 and 75 modified with iron or zinc of 1, 5 or 10 wt.% by wet impregnation method). In case of materials BETA Si/Al 38 and 75 led material impregnation with metal to increase of material catalytic activity (accompanied with increase of amount of weak acid sites detected using temperature programmed desorption). Material BETA 38 with loading 1 wt.% of Fe provided 97% citronellal conversion and 94% selectivity of isopulegol formation (90 °C, toluene, 24 h).

### **Graphic Abstract**



Keywords Isopulegol · Fe-BETA zeolite · Citronellal cyclization · Prins cyclization · Heterogeneous catalysis

# 1 Introduction

Isopulegol is a well-known and important monoterpene alcohol, which can be obtained as a product of citronellal cyclization, is often used in a fragrance industry as a part of blossom composition fragrances, and is an important

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intermediate for menthol synthesis. Menthol (with characteristic peppermint odor) is further used as an important ingredient in various pharmaceuticals, cosmetics and special products [1–3]. Citronellal, which serves as a main source for obtaining isopulegol, is renewable compound, abundantly present in a large number of essential oils (e.g. lemongrass). Process of citronellal cyclization might be catalyzed, either homogeneously or heterogeneously. In the second half of the twentieth century, the usage of the especially homogeneous catalysts was studied. As homogeneous catalysts tris(triphenylphosphine)rhodium [4], molybdenum or tungsten carbonyl complexes [5] are

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reported to be used. As another efficient catalyst scandium trifluoromethanesulfonate was reported (under low temperature (-78 °C) [6]). Traditional Lewis acids as ZnCl<sub>2</sub>, ZnBr<sub>2</sub>, AlCl<sub>3</sub>, SbCl<sub>3</sub>, SnCl<sub>4</sub> and TiCl<sub>4</sub> might be also used for cyclization of citronellal [7]. Heterogeneous catalysts are also widely reported to be used for this cyclization, since they can offer some advantages, as avoiding handling corrosive mixtures and producing large amounts of waste water or can offer possibility of catalyst reuse. Study [8] described the use of solid materials SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, FeSO<sub>4</sub>, NiSO<sub>4</sub>,  $Ti(SO_4)_2$ ,  $Zr(SO_4)_2$  and  $Al_2O_3$ , which did not decompose by hydrolysis (compared to traditional Lewis acids) and led to the conversion 61-90% with selectivity higher than 90%. Citronellal cyclization was also led in gas phase on ion-exchanged faujasites [9]. Another used catalysts were based on ZrO<sub>2</sub> or its sulphated alternatives (99% citronellal conversion, 99% selectivity of isopulegol formation) [10]. In study [11] Zr-impregnated  $\beta$ -zeolites were used with maximum impregnated amount 2.4 wt.% of Zr. Another possible catalysts were zeolite ZSM-5 in benzene (total citronellal conversion, >97% selectivity of isopulegol formation) [12], mixed oxides as  $TiO_2$ -(SiO<sub>2</sub>)<sub>x</sub>, ZrO<sub>2</sub>-(SiO<sub>2</sub>)<sub>x</sub> [13] or mixed gels HfO<sub>2</sub>-(SiO<sub>2</sub>)<sub>8</sub> [14]. Using of BETA zeolites with low Si/Al ratio was reported with high citronellal conversion (>99%) and >95% selectivity of isopulegol formation [15, 16]. Silica or MCM-41 modified with phosphothungstic acid can be also used to catalyze this reaction (>97% citronellal conversion, >74% selectivity of isopulegol formation) [17, 18]. Most recently,  $WO_3$ -SiO<sub>2</sub> materials are reported to be used in this reaction [19].

Fe-modified zeolites BETA are known for its catalytic activity and were recently used e.g. in perillyl alcohol preparation from  $\beta$ -pinene oxide, with the range of impregnated iron from 0 to 10 wt.% [20]. In another study [21] the authors used  $\beta$ -zeolites modified by iron for  $\alpha$ -pinene isomerization to important substance *trans*-carveol. In this case  $\beta$ -zeolites were modified with 0.625–10 wt.% Fe.

In this work we would like to present catalytic activity of iron and zinc modified  $\beta$ -zeolites with Si/Al molar ratio 25, 38 and 75. The influence of these metals on the course of citronellal cyclization was not previously described. Iron and as well zinc are available, cheap and efficient catalysts in many acid catalyzed reactions.

# 2 Experimental

# 2.1 Materials

Int. For zeolite modifications  $Fe(NO_3)_3 \cdot 9H_2O$  from Lachema and  $Zn(NO_3)_2 \cdot 6H_2O$  from Lach-Ner (both p.a.) were used.

# 2.2 Catalyst Preparation

Fe- and Zn- modified zeolites were prepared as described in [20]. Zeolite (1 g) was modified with 1, 5 or 10 wt.% of metal by wet impregnation method. In 15 cm<sup>3</sup> of demineralized water the needed amount of metal nitrate was dissolved and then 1 g of zeolite was added. The suspension was stirred for 12 h at 60 °C. After that, water was evaporated and modified zeolite was dried overnight at 100 °C. Material was then calcined (450 °C, air, 12 h). Materials were denoted with names according to  $\beta$ -zeolite type and Fe/ Zn amount used (e.g. BE25Fe1 – material BETA25 modified with 1 wt.% of Fe).

# 2.3 Catalyst Characterization

Prepared catalysts were characterized using different methods. Non-modified and modified materials were analyzed on UV-VIS Spectrometer Lambda 35 (Perkin Elmer). XRD powder data was measured at RT on  $\theta$ - $\theta$  powder diffractometer X'Pert PRO in Bragg-Brentan parafocusing geometry with CoK $\alpha$  radiation ( $\lambda = 1.7903$  Å, U=35 kV, I=40 mA). XRF analysis was performed on WD-XRF ARL 9400 XP Spectrometer. The specific surface area was determined using nitrogen adsorption (3Flex volumetric analyzer, Micromeritics, USA). The specific surface area of materials was calculated via the BET equation and t-plot method. Temperature-programmed desorption (TPD) of pyridine was measured on AutoChem II 2920 (Micromeritics, USA). Details of TPD measurement were provided in our previous works [19, 22]. Powders for SEM analysis were applied on carbon adhesive tape and then goldened by 5 nm of gold via Quorum Q150 ES (Quorum Technologies Ltd., Laughton, UK). Footage were made 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 mod BSE. For elemental analysis, EDS analyzer OXFORD Instrument X-max 20 mm<sup>2</sup> with software Aztec (Oxford Instruments, Abingdon, UK) was used.

# 2.4 Typical Experiment

Catalyst (5 wt.% to citronellal) was inserted into round bottom 25 cm<sup>3</sup> flask with magnetic stirrer and then 3 cm<sup>3</sup> of toluene was added. Suspension was stirred and heated to 50 °C and then 1 g of citronellal was added and reaction continued at 50 °C for 24 h. Hot filtration test was used to confirm that reaction is only heterogeneous catalyzed – reaction was carried out using typical reaction conditions for 30 min, then the catalyst was separated from the reaction mixture and this mixture was heated for 24 h. The fact, that the reaction did not take place after catalyst removal confirmed heterogeneity of this reaction. Analysis of product from citronellal cyclization was performed on gas chromatograph Shimadzu GC-17A, equipped with polar column Stabil Wax with length 30 m, inner diameter 0.32 mm and thickness of stationary phase 0.5 µm. Carrier gas was helium. Citronellal conversion ( $x_{citronellal}$ ) and selectivity of isopulegol ( $s_{isopulegol}$ ) formation were calculated according to Eqs. 1 and 2.

$$x_{citronellal} = \frac{rel.concentration_{citronellal}}{initial \ rel.concentration_{citronellal}} \times 100 \tag{1}$$

Equation 1 Calculation of citronellal conversion (x)

$$s_{isopulegol} = \frac{rel.concentration_{isopulegol}}{x_{citronellal}}$$
(2)

Equation 2 Calculation of selectivity of isopulegol formation.

# **3** Results and Discussion

#### 3.1 Material Characterization

X-Ray fluorescence (XRF) was performed to determine the composition of prepared materials (Table 1). Fe/Zn content calculated from XRF results showed to be in good correlation with desired amount of metal in the prepared materials (1, 5 or 10 wt.%).

Table 1 XRF results showing catalyst composition (wt.%)

Catalyst	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> (ZnO <sup>a</sup> )	Others	Fe (Zn <sup>a</sup> ) (calcu- lated)
BE25Fe1	91.3	6.8	1.8	0.1	1.3
BE25Fe5	85.9	6.3	7.7	0.1	5.4
BE25Fe10	81.1	5.9	13.0	0.1	9.1
BE25Zn5	86.7	7.0	6.0 <sup>a</sup>	0.3	4.8 <sup>a</sup>
BE38Fe1	93.5	4.6	1.8	0.1	1.3
BE38Fe5	87.7	4.2	8.0	0.1	5.6
BE38Fe10	82.2	4.0	13.8	0.1	9.7
BE38Zn5	88.5	4.3	7.1 <sup>a</sup>	0.2	5.7 <sup>a</sup>
BE75Fe1	96.7	1.4	1.6	0.3	1.1
BE75Fe5	90.1	1.4	8.2	0.3	5.7
BE75Fe10	84.3	1.3	14.1	0.3	9.9

<sup>a</sup>ZnO/Zn content

#### 3.2 X-Ray Diffraction

X-Ray diffraction was used to confirm the catalyst structure (Fig. 1). In the case of pure BETA38 material characteristic bands for zeolite were observed – 7.9, 16.8, 17.9, 21.6, 22.6, 25.5, 27.0, 29.0, 30.0, 33.6, 34.9 and 44.0 2Theta°. These bands were present also in the case of Fe or Zn modified materials, which confirmed the fact, that incorporating Fe/Zn ion into the zeolite did not destroyed its structure. In BE38Fe1 material characteristic bands for iron oxides were not present, which could mean, that their intensity was either bellow detection limit or iron oxide was homogeneously distributed in zeolite material. In the case of BE38FE5 and BETA38Fe10 several bands characteristic for  $Fe_2O_3 - 35.6$ , 40.9 and 49.5 2Theta° and  $Fe_3O_4$ - 30.5, 37.4, 53.8 and 66.3 2Theta° were present [23, 24]. In the case of Zn modified material the zeolite structure was not affected, which fact was already described in literature [25].

#### 3.3 Diffuse UV–VIS Reflectance

UV–VIS spectra for Fe-modified zeolites showed characteristic local maxima at 420 nm and 890 nm, which intensity increased with increasing Fe-loading (Fig. 2). The significant reflectance increase was also observed in the area of 500–600 nm with increasing metal loading. The band in area 400–450 nm can be assigned to Fe-OH interaction, 500–600 nm to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and 850–900 nm to  $\alpha$ -Fe-OOH interaction [20, 26]. Spectra of BE38Zn5 material did not have any specific maxima, only in the range of 300–600 nm a significant decrease of reflectance was observed compared to nonmodified BETA38.



Fig. 1 XRD diffractograms of nonmodified BETA38 and this material modified with different Fe/Zn loading



Fig. 2 UV–VIS spectra for nonmodified BETA38 and this material modified with different Fe/Zn loading

# 3.4 Temperature Programmed Desorption of Pyridine

Temperature programmed desorption of pyridine was performed to determine the acidity of prepared materials (Table 2).

All materials contained two temperature maxima representing weak and strong acid sites (Table 2, Fig. 3). In the case of BETA25 and BETA38 a significant decrease in the material acidity was observed after modification. On the other hand, in the case of BETA75, the increase of acidity was observed using 1 and 5 wt.% of Fe. This phenomenon was probably caused by fact, that BETA75 possessed by only low acidity itself, because it has the highest Si/Al ratio from

 Table 2
 Characterization of materials obtained using temperature programmed desorption of pyridine

	T <sub>max</sub> 1 (°C)	T <sub>max</sub> 2 (°C)	Acid sites $n_{ads}^{pyridine}$ (µmol. $g_{cat}^{-1}$ )		ads
			Σ	Weak	Strong
BETA38	245	617	821	318	503
BE38Fe1	254	566	604	388	215
BE38Fe5	252	510	488	331	157
BE38Fe10	249	501	390	272	118
BETA25	257	606	2229	432	1797
BE25Fe1	249	567	540	358	182
BE25Fe5	267	511	455	284	171
BE25Fe10	251	533	406	253	153
BETA75	241	578	198	162	35
BE75Fe1	245	498	227	166	61
BE75Fe5	253	504	220	155	65
BE75Fe10	239	499	169	133	35



Fig.3 TPD-MS signal for (non)modified BETA38 (m/z=79 fragment)

all studied BETA materials. Therefore using certain Fe loading had a positive effect on the material acidity. Too high amount of Fe probably caused the blockage of the pores and decrease the availability of acid sites for acidity measurement. The effect of modification, visible in case of BETA25 and BETA38 above all, was caused by the fact, that a significant decrease in number of strong acid sites occurred after modification. In all cases of modified materials, the acidity decreased with higher Fe loading. This could be caused by the fact, that using higher Fe loading resulted in significant crystallite of iron oxides formation, which could cause partial pore blockage as mentioned above.

#### 3.5 Nitrogen Physisorption

Table 3 summarizes the results of the textural analyses of the catalysts. All samples of catalysts contain a mixture of micropores and mesopores, but the samples differ in the ratio of micropores and mesopores. The total pore volume of pores less than 40- nm diameter at  $p/p^\circ = 0.95$  (V<sub>total</sub>) of catalysts was found in the range from 0.31 to 0.34 cm<sup>3</sup> g<sup>-1</sup>, but the micropore volume (t-plot method) was in the range from 0.18<sup>1</sup> to 0.21 cm<sup>3</sup> g<sup>-1</sup>. Modification of material with iron or zinc led to decrease of total micropore volume. Modification of zeolite with different iron loading > 5 wt.% resulted in decrease of specific surface area (using 10 wt.% of iron led to decrease from 540 to 483 m<sup>2</sup>/g which equals to total 10% decrease of total specific surface area).

All samples of catalysts show adsorption isotherms of type Ib and IVa (IUPAC classification), so samples consist of micropores and mesopores with classical type hysteresis loop H1 (IUPAC classification), which corresponds to narrow range of uniform mesopores. Figure 4 shows the  $N_2$ 

Table 3 Textural characteristic

of catalysts

	S <sub>BET</sub> m <sup>2</sup> /g	S <sub>t-plot</sub> m <sup>2</sup> /g	Total Pore vol- ume cm <sup>3</sup> /g	t-Plot micropore volume cm <sup>3</sup> /g	Ratio of micropores (%)
BETA38	540	136.2	0.34	0.21	63.4
BE38Fe1	543	145.1	0.34	0.21	60.8
BE38Fe5	493	117.5	0.32	0.20	60.7
BE38Fe10	483	115.0	0.31	0.19	59.5
BE38Zn5	503	144.8	0.31	0.18	58.8



Fig. 4 Nitrogen physisorption isotherms for (non)modified BETA38 zeolite

(77 K) adsorption and desorption isotherms (red and black symbols) for all samples.

#### 3.6 Scanning Electron Microscopy (SEM)

SEM image for BETA38Fe5 (Fig. 5) with element mapping images showed homogeneous distribution of Fe on catalyst surface.

### 3.7 Catalytic Testing

Prepared materials were used as catalysts in intramolecular Prins reaction – citronellal cyclization forming isopulegol as a desired product (Fig. 6) to evaluate their catalytic activity. In all reactions a high selectivity of isopulegol formation (>95%) was observed, the only identified byproduct was a product of citronellal autocondensation.

Activity of nonmodified BETA zeolites with different Si/Al ratio was compared (Fig. 7). The most active material in citronellal cyclization was shown to be zeolite BETA25. BETA25 material possessed by the lowest Si/Al ratio, which means that it was the most acidic one from the studied zeolite BETAs (its highest acidity was also confirmed by TPD measurement). Mentioned acidity significantly influenced catalyst activity as it is visible from Fig. 7 – the increase of acidity lead to increase of the achieved citronellal conversion after 24 h.



**Fig.5** SEM image of BE38Fe5 material and element mapping images for Fe and Si (magnification 1000x)

Activity of Fe and Zn modified zeolite BETA25 was tested (Fig. 8) flowingly.

From graph (Fig. 8) it is clear, that modified materials were significantly less efficient in citronellal cyclization comparing the nonmodified BETA25. In both cases with increasing modificator amount, the decrease of catalytic activity was observed. This is in correlation with TPD results for Fe modified materials (Table 2) where a notable decrease in acidity was observed after modification. Comparing the same modificator amount in case of Fe or Zn modification – the more considerable decrease of material activity was observed in the case of Zn-modified materials. From studied zeolites BETA (25, 38 and 75), BETA25 has the highest number of acid sites and its modification could cause blocking of these acid sites, which could induce above mentioned decrease of activity after its modification.

Activity of pure zeolite BETA38 was notably lower compared to BETA25 material (Fig. 9). In the case of BETA38 material the modification was advantageous - material activity increased after modification in the case of all Fe-loading and in case of Zn 1 wt.% metal loading. The behavior of Fe modified BETA38 was surprising looking at the total acidity of the materials. The decrease of the acidity after modification of pure BETA38 was observed (Table 2). Nevertheless, the amount of weak acid sites increased after modification. This might lead to the conclusion that in the citronellal cyclization participates mainly weak acid sites. On the other side, the role may also play a fact the availability of acid sites. In the case of nonmodified BETA38 the sites responsible for acidity are incorporated in the catalyst pores mainly. In Fe modified catalysts, the decreased specific surface confirmed the partial pore blockage by the Fe oxide particles. These particles are probably more accessible for catalysis.

Both Fe and Zn modified BETA38 with 1 wt.% of metal exhibited significantly higher activity than nonmodified zeolite (Table 4). Fe-modified materials with metal loading 5 and 10 wt. % showed also higher activity than using nonmodifed zeolite. On contrary in case of Zn-modified materials using of 5 or 10 wt.% metal loading was disadvantageous and lead to lower citronellal conversion than using nonmodified zeolite (Table 4). Lower activity of BE38Zn1 compared to BE38Fe1 can be explained by the fact, that Zn is weaker Lewis acid compared to Fe. Comparing the influence of total acidity of Fe and Zn modified materials on achieved conversion the expected trend in the case of Zn modified materials was observed. With increasing material



Fig. 6 Reaction scheme of isopulegol formation (a-isopulegol; b-autocondensate of citronellal)

**Fig. 7** Isopulegol concentration using different nonmodified zeolites BETA(left) and influence of material acidity on citronellal conversion at 24 h of reaction (right); (3 cm<sup>3</sup> toluene, 1 g (1.17 cm<sup>3</sup>) citronellal, 0.05 g catalyst, 50 °C)



**Fig. 8** Isopulegol concentration using different Fe-modified (left) and Zn-modified (right) zeolite BETA25 (3 cm<sup>3</sup> toluene, 1 g (1.17 cm<sup>3</sup>) citronellal, 0.05 g catalyst, 50 °C)

acidity, the achieved conversion also increased. The different was the behavior of Fe modified BETA. As the material with 1% loading was the most acidic of all three compared, it was also the most active. The other two materials achieved comparable conversion (and the reaction course was almost the same) although their acidity was different. In this case, the specific surface (that was almost the same for both of these materials) played a main role.

Activity of zeolite BETA75 modified by different Fe loading was also tested (Fig. 10). In this case, the same trend





Table 4 Citronellal conversion using BETA38 based materials (3 cm<sup>3</sup> toluene, 1 g (1.17 cm<sup>3</sup>) citronellal, 0.05 g catalyst, 50 °C, 24 h)

Material	BE38	BE38Fe1	BE38Fe5	BE38Fe10	BE38Zn1	BE38Zn5	BE38Zn10
Conversion (%)	30	68	45	47	47	26	21

as using modified BETA38 was observed – the highest activity was obtained using BE75Fe1 material, activity of BE75Fe5 and BE75Fe10 was lower comparing the material with 1 wt.% of Fe, but still higher than nonmodified zeolite. Higher Fe loading resulted in lower material acidity and this was connected with lower catalytic activity of the material (Fig. 10).

BETA38 and BETA75 have higher Si/Al ratio compared to BETA25 with the resulting lower material acidity. Modification using 1 wt.% of Fe can add acid sites, which results in higher catalytic activity of materials. In case of 5 or 10 wt.% of Fe crystallites are formed, which can cause the pore blocking accompanied by material loss of activity compared to material with only 1 wt.% metal loading.

Selectivity of isopulegol formation was in all cases > 94%and was not dependent on material acidity (Fig. 11) or on citronellal conversion.

Influence of used solvent on the reaction course was tested using BE38Fe1 material (Table 5).

In the case of different solvents, selectivity of isopulegol formation decreased by the formation of citronellal autocondensate or ethoxycitronellal in case of solvent ethanol. N,N'-Dimethylformamide, dimethylsulfoxide, acetonitrile and *N*-methylpyrrolidone were not suitable solvents for citronellal cyclization – only low conversions were obtained after 24 h (10–39%). This may be explained by the fact, that all these solvents belong to the group of aprotic basic solvents represented by high or medium donor number. Low conversions might be caused by the blockage of acid sites of catalyst by the solvents. The high basicity may also explain the lower selectivity to isopulegol formation. In basic media citronellal autocondensation may occur more probably. The highest selectivity of isopulegol formation was obtained using toluene (99%) and heptane (95%) – non-polar non-basic solvents.

Influence of reaction temperature on reaction course was tested (Table 6). As expected, reaction rate increased with increasing temperature. Selectivity of isopulegol formation was not dependent on temperature and was in the range 93 - 98%.

#### 3.8 Comparison with Data in Literature

Comparison with published data was performed (Table 7). Fe-modified BETA zeolite showed to be cheap alternative **Fig. 10** Isopulegol concentration using different Fe-modified zeolite BETA75(left) and citronellal conversion dependence on material acidity (right) (3 cm<sup>3</sup> toluene, 1 g (1.17 cm<sup>3</sup>) citronellal, 0.05 g catalyst, 50 °C)



Fig. 11 Selectivity of isopulegol (24 h) formation based on catalyst acidity (left) and dependence of selectivity on conversion (right) using materials with 1 wt.% Fe (3 cm<sup>3</sup> toluene, 1 g (1.17 cm<sup>3</sup>) citronellal, 0.05 g catalyst, 50 °C)



 Table 5
 Influence of used solvent on reaction course (24 h, 3 cm<sup>3</sup> solvent, 1 g (1.17 cm<sup>3</sup>) citronellal, 0.05 g catalyst BE38Fe1, 50 °C)

Solvent	DMF	DMSO	ACN	NMP	Heptane	Toluene	1,4-dioxane	Acetone	Ethanol
Citronellal conversion (%)	10	13	26	39	53	68	97	98	98
Selectivity of isopulegol formation (%)	51	82	82	82	95	99	89	51	77

DMF N,N-dimethylformamide, DMSO dimethylsulfoxide, ACN acetonitrile, NMP N-methylpyrrolidone

**Table 6** Influence of temperature on reaction course  $(24 \text{ h}, 3 \text{ cm}^3 \text{ tol-uene}, 1 \text{ g} (1.17 \text{ cm}^3)$  citronellal, 0.1 g catalyst BE38Fe5)

Temperature (°C)	50	70	90
Citronellal conversion (%)	68	89	98
Selectivity	99	94	94

providing both high conversion and selectivity to already tested heterogeneous catalysts.

# 4 Conclusion

Several zeolite BETAs modified with different metal loadings were prepared and intensively characterized. X-Ray diffraction confirmed that zeolite structure was preserved after modification and X-ray fluorescence confirmed the desired metal loading. Acidity of materials was measured using temperature programmed desorption of pyridine and it was shown that in order 10 < 5 < 1 wt.% Fe loading materials acidity increased. This acidity increase was in accordance with material catalytic activity increase. Modified zeolites BETA possessed by high selectivity of isopulegol formation (>93% in all cases). In the case of zeolites BETA38 and BETA75, the increase of catalytic activity was observed after materials modification with Fe. On the other hand, the same modification in case of BETA25 zeolite lead to decrease of material catalytic activity. Material BETA 38 with loading 1 wt.% of Fe was used to optimize the reaction conditions - using temperature 90 °C, 5 wt.% of catalyst, 1 g of citronellal and  $3 \text{ cm}^3$  of toluene – 97% citronellal conversion and 94% selectivity of isopulegol formation (24 h) was obtained, which showed that this catalyst can be successfully used in the studied reaction. The higher catalytic activity of Fe-modified BETA38 zeolite compared to BETA75 can be attributed to its higher material acidity, which has a positive effect on the reaction course.

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Reference	Catalyst	Citronellal conversion (%)	Selectivity of isopulegol forma- tion (%)	Time (h)	Reaction conditions
Current work	Fe-BETA (Si/Al=25)	99	96	5	90 °C, 5wt.% of cat., CA 1 g, 3 cm <sup>3</sup> of toluene
Current work	Fe-BETA (Si/Al=38)	98	94	24	90 °C, 5wt.% of cat., CA 1 g, $3 \text{ cm}^3$ of toluene
da Silva [17]	$\mathrm{H_{3}PW_{12}O_{40}/SiO_{2}}$	97	98	0.5	25 °C, 1wt.% of cat., CA 0.15 mmol, cyclohexane
Braga et al. 18]	20%HPW/MCM-41	100	74	3	25 °C, CA 1 mmol, 10 wt% of cat., 5 cm <sup>3</sup> CH <sub>2</sub> Cl <sub>2</sub>
Mäki-Arvela et al. [15]	H-Beta-11	100	95	3	90 °C in cyclohexane, CA 3 g, 200 mg cat
Shah et al. [27]	ZSM-5	80	95	1	60 °C, CA 4.5 mmol, 5 cm <sup>3</sup> benzene, 0.1 g cat
Rasero-Almansa and Sánchez [28]	Zr(Ti)MOF	99	76	24	150 °C in cyclohexane, CA 0.3 mmol, 5 mg cat
Plößer et al. [16]	H-BEA (Si/Al=25, 35, 150)	99	98	1	80 °C, CA 0.5 cm <sup>3</sup> , 50 mg cat., 10 cm <sup>3</sup> hexane
Vrbková et al. [19]	WO <sub>3</sub> -SiO <sub>2</sub>	91	97	24	50 °C, 10wt.% of cat., CA 1 g, $3 \text{ cm}^3$ of toluene

# **Compliance with Ethical Standards**

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

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