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# Biomass to chemicals: Rearrangement of $\beta$ -pinene epoxide into myrtanal with well-defined single-site substituted molecular sieves as reusable solid Lewis-acid catalysts

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#### ABSTRACT

The epoxide rearrangement of  $\beta$ -pinene oxide into myrtanal was studied in the presence of solid Lewisacid catalysts. Different metals such as Zr, Sn, Ti, Nb, Ta, Al, and Ga have been incorporated within network positions of zeolite Beta by isomorphous substitution. The materials have been characterized by powdered X-ray diffraction (XRD), IR spectroscopy and by in situ IR spectroscopy on adsorbed molecules (cyclohexanone and pyridine). Among the studied catalysts Zr-Beta gave the best selectivity (up to 94%) in acetonitrile as solvent at practically complete conversion. In this epoxide rearrangement the solvent has to be selected to balance the competitive adsorption of the product. Product desorption is enhanced with acetonitrile which results in a selectivity increase with only a small penalty on the rate of reaction. Zr-Beta has been reused in the batch mode and in a fixed-bed reactor for several times and analysis of the reused catalyst indicated that Zr-Beta is a robust catalyst for the epoxide rearrangement. Leaching of the metal or crystal degradation has not been detected.

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### 1. Introduction

The development of reusable solid catalysts with isolated and well-defined single sites is a matter of scientific and industrial interest to achieve good activities and selectivities [1,2]. Zeolites are very convenient materials to design single or multisite catalysts, since well-defined Brönsted and Lewis acids (metals) can be introduced within framework positions. The electronic characteristics of these sites as well as the adsorption characteristics of the material can be modulated during the synthesis or even by postsynthesis treatments to adapt the solid to the specific reaction to be catalyzed.

The catalytic activity of Brönsted acids can be correlated with their ability to form acid-base adducts through proton transfer. In contrast, in the case of zeolites with Lewis-acid sites the molecular interaction depends on several parameters [3] such as: the intrinsic acid strength (measured as the energy of the lowest unoccupied molecular orbital-LUMO), a back-donation of electron density from the Lewis acid to the empty orbitals of the base, and changes in the electronic levels of the active site caused by its interaction with the reactant molecules.

The relative importance of the different parameters involved in the catalytic phenomena with Lewis-acid sites dictates why some Lewis-acid catalysts are effective for one reaction and show no

activity for others. For instance, materials involving titanium sites incorporated into a siliceous zeolite as can be titanium silicalite-1 (TS-1) or Ti-Beta, are excellent catalysts for the activation of hydrogen peroxide on the metal to perform olefin epoxidation reactions [4], while the metal active site of Sn-Beta does not activate hydrogen peroxide, but interacts with a carbonyl group of the reactant molecule by accepting electron density. However, this electron density is not transferred into empty orbitals of the tin center but into anti-bonding molecular orbitals centered at the adjacent oxygen atoms [5]. With the help of this additional electron density hydrogen peroxide can be bound to these oxygen atoms via hydrogen bonding. Both reactants adsorbed onto the zeolite constitute a perfect starting point for the Baeyer-Villiger (BV) oxidation of the carbonyl compound (see Fig. 1). Thus, although both metals, Ti and Sn, are tetra-valent Lewis acids and have isomorphically substituted silicon atoms in the same zeolite framework, the catalytic activity of the titanium material is excellent for olefin epoxidation and very poor for the BV oxidation. On the other hand, the activity of Sn-Beta for epoxidations with hydrogen peroxide is negligible while it performs very well the BV oxidation of cyclic ketones.

If we now select a third type of reaction which is also catalyzed by Lewis acids, i.e. the Meerwein-Ponndorf-Verley (MPV) reduction [6], it has been observed that the catalytic performance of different metal substituted zeolites can change with the type of substrate. When cyclohexanone was contacted with 2-butanol, Sn-Beta gave a four-fold activity with respect to Zr-Beta, whereas the activity was almost inverse for the mixture benzaldehyde/2-

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**Fig. 1.** Energy of the LUMO of the metal complexes with cyclohexanone coordinated to the metal and hydrogen peroxide to the adjacent oxygen atom of the hydroxy group calculated for the Ti-Beta and the Sn-Beta catalyst. For Sn-Beta the LUMO is the  $\pi$  anti-bonding orbital of the carbonyl group that can be attacked by the HOMO of the hydrogen peroxide. For Ti-Beta the LUMO is located at the metal and therefore the hydrogen peroxide tends to coordinate to the metal instead of attacking the carbonyl bond.

butanol [3]. From the examples given above, plus much results reported in the literature on Lewis-acid reactivity [2,7,8], it appears difficult to predict a priori or by simple analogy the best active site for a given reaction.

Recently we have shown that Lewis acids can be used for the transformation of biomass into fine chemical products [9,10]. Myrtanal has been isolated from natural products, such as the roots of Greek *Paeonia* taxa among others [11]. These plants have been used through antiquity, as antiseptic and for cleansing wounds. Up to 25% of myrtanal was found in essential oils from Geum urbanum roots [12]. Synthetically it has been obtained from  $\beta$ -pinene oxide with 45% yield using solid catalysts such as aluminium oxides [13].

Owing to the industrial interest of the reaction, we have studied here the possibilities of metal zeolites with well-defined single isolated sites, to catalyze the synthesis of myrtanal from  $\beta$ -pinene oxide by epoxide rearrangement (Eq. (1)).



It will be shown that by properly selecting the catalyst and reaction conditions it is possible to achieve 94% yield of the desired myrtanal product which is much higher than any other value reported up to now.

#### 2. Experimental

#### 2.1. Catalyst preparation and characterization

The syntheses of metal-containing zeolite Beta materials were performed in fluoride medium from gels of the following composition [14]:

# SiO<sub>2</sub>:xM : 0.54TEAOH : 0.54HF :yH<sub>2</sub>O

where *x* was 0.01 or 0.02, and *y* was varied between 4 and 7. The reactants were zirconyl chloride, Sn(IV) chloride pentahydrate, Ti(IV), Nb(V) and Ta(V) ethoxides, Al(III) isopropoxide, and Ga(III) nitrate as different metal sources and for all zeolites in common tetraethylorthosilicate as the silica source, tetraethylammonium hydroxide (TEAOH, 35 wt% in water) and HF (50 wt% in water). Dealuminated zeolite Beta seeds were also employed for the synthesis. The crystallization was carried out in Teflon-lined stainless-steel autoclaves at 140 °C under rotation for different periods of time. After the desired time, the autoclaves were cooled down to room temperature and the zeolites were collected by filtration, washed with water and dried at 100 °C overnight. The as-synthesized metal-containing zeolite Beta materials were calcined in static air at 580 °C for 3 h in an oven in order to remove the occluded organic.

Crystallinity and phase identification of the materials was done by powder X-ray diffraction (XRD) in a PANalytical CUBIX diffractometer equipped with a PW3050 goniometer (Cu K $\alpha$  radiation) provided with a variable divergence slit. The metal content of the as-synthesized and calcined samples was determined by chemical analysis (Varian 715-ES ICP-Optical Emission Spectrometer) after dissolution of the solids in a HNO<sub>3</sub>/HF solution. The following silicon/metal ratios were determined: Si/Zr = 130 and 115, Si/Sn = 130, Si/Ti = 132, Si/Nb = 109, Si/Ta = 78, Si/Ga = 45, and Si/Al = 103. The XRD patterns of the calcined samples (580 °C/3 h) confirmed high crystallinity and peaks of the corresponding metal oxides were not observed (patterns not shown). Nitrogen adsorption experiments on the calcined samples (580 °C/3 h) gave an isotherm very similar to that of pure silica-Beta with micropore volumes of 0.20–0.21 cm<sup>3</sup> g<sup>-1</sup> and BET surface areas of 450–475 m<sup>2</sup> g<sup>-1</sup>.

#### 2.2. Metal characterization

In order to ascertain the metal coordination and consequently to support their location in framework positions the following techniques were used: UV–visible DR for Ti (not shown) and EXAFS-XANES for Sn, Nb, and Ta. The Lewis acidity was evidenced by adsorption–desorption of pyridine and/or cyclohexanone followed by IR spectroscopy.

Infrared (IR) measurements were performed with a Nicolet 710 FTIR spectrometer using vacuum cells. The spectra in the framework vibration region were done using the KBr pellet technique, whereas experiments with adsorption of pyridine and cyclohexanone as probe molecules were performed in self supported wafers of 10 mg cm<sup>-2</sup> that were degassed overnight under vacuum ( $10^{-2}$  to  $10^{-3}$  Pa) at 400 °C. The spectra were recorded and then pyridine or cyclohexanone was admitted and, after equilibration, the samples were outgassed for 1 h at increasing temperatures ( $150/250/350 \circ$ C for pyridine and  $25/50/100/200 \circ$ C for cyclohexanone). After each desorption step, the spectrum was recorded at room temperature and the background subtracted in the pyridine case.

#### 2.3. Catalytic reaction

 $\beta$ -Pinene oxide was prepared by a standard epoxidation method and was employed in 96% purity (<sup>1</sup>H NMR). 600 mg of the epoxide was dissolved in 3 g of solvent. A 50-mg sample of the catalyst was added and the reaction mixture heated to 80 °C while stirring. The reaction was monitored by gas chromatography with a Varian 3900 GC equipped with a Carbowax column (15 m length, 0.32 mm inner diameter and 0.25  $\mu$ m film).

Myrtanal was identified by mass spectroscopy and NMR spectroscopy on a sample distilled from the reaction mixture: MS m/z (%): 152(2) [M]<sup>+</sup>, 29(47), 39(58), 41(100), 67(91), 69(80), 81(70), 82(63), 83(37), 123(54); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 204.0, 49.0, 40.5, 40.2, 39.4, 26.2, 23.9, 23.5, 20.4, 12.9.

For the recycling tests in the batch mode 6.00 g of the epoxide in 30 g of acetonitrile solvent and 500 mg of the Zr-Beta catalyst were heated to 80 °C for 2 h. The reaction mixture was filtered and the recovered solid catalyst re-activated by calcination at 580 °C for 3 h. For the subsequent cycle the amount of solvent and epoxide were scaled to the available quantity of catalyst. After 8 recycles 50% of the catalyst had been lost due to the catalyst handling (6.25% on an average per cycle). The crude reaction mixtures were analyzed as described above.

For the fixed-bed continuous-flow reactor study Zr-Beta-2 was pelletized and sieved (0.4–0.6 mm) and 800 mg of the catalyst placed in a stainless-steel tube (14 cm, 4 mm inner diameter). The reactor tube was heated to 80 °C and the feed (17 wt% of  $\beta$ -pinene oxide in acetonitrile) was passed at a rate of 0.5 mL/min that corresponded to a weight hourly space velocity (WHSV) of 30 h<sup>-1</sup> and a contact time of 2 min. The product was collected at the end of the reactor at room temperature. When the conversion started to decrease the reaction was stopped and the catalyst re-activated by passing an air flow (30 mL/min) at 500 °C for 20 min. After cooling down to 80 °C the reaction was continued. The crude reaction mixtures were analyzed off-line as described above.

# 3. Results and discussion

# 3.1. Catalyst characterization

All Beta catalysts were synthesized with hydrogen fluoride as mineralizer and were activated by calcination in air (3 h, 580 °C). The zeolite structure was confirmed by powdered X-ray diffraction, and the incorporation of the metal into crystallographic network positions has been demonstrated before by extended Xray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES), working with Ti [15], Sn [16], Nb [17], and Ta [17] substituted Beta samples. In the original papers it has been shown that when the metals were incorporated into the zeolite framework, the resultant zeolites present Lewis acidity as demonstrated by adsorption of a probe molecule (cyclohexanone; cf. Fig. 2) for the metal substituted samples used in this work. Additionally, as a fast and simple rejection technique we have used IR spectroscopy since the spectra of metal substituted zeolites show a band at 960  $\rm cm^{-1}$  (not shown). In other words, the presence of a band at 960 cm<sup>-1</sup> is a necessary fact if a metal is incorporated, but it is not sufficient to ascertain the incorporation [15,18,19].

For comparison purposes we have also prepared the Beta aluminosilicate (Si/Al = 103) and a Ga silicate (Si/Ga = 45). These samples show both Lewis and Brönsted as evidenced by pyridine adsorption and IR spectroscopy (see Fig. 3).

### 3.2. Activity tests

In a preliminary screening we have seen here that Zr-Beta, Sn-Beta, and Ti-Beta give high catalytic activity for this reaction and therefore these three solids have been chosen to study the influence of the nature of solvents. Hence,  $\beta$ -pinene oxide was dissolved in different solvents and contacted with the three Lewis-acidic Beta-



wavenumber (cm<sup>-1</sup>)

**Fig. 2.** In situ infrared spectra of cyclohexanone adsorbed onto different Beta zeolites. In the figure the corresponding spectra are displayed after zeolite activation (straight line), after desorption at 100 °C (dash line) and after desorption at 200 °C (dash dot line; 150 °C for Zr-Beta).



**Fig. 3.** In situ infrared spectra (a) of the hydroxide region of Al-Beta and Ga-Beta before adsorption of pyridine (thick line) and after adsorption of pyridine and desorption at 150 °C (thin line) and (b) of the difference for pyridine adsorbed onto Al-Beta and Ga-Beta after desorption at 150 °C and the corresponding zeolite background spectra.

zeolites, i.e. Zr-Beta, Sn-Beta, and Ti-Beta. The best selectivity was observed with the Zr-Beta catalyst in acetonitrile solvent (Table 1, entry 1). At a reaction temperature of  $80 \,^{\circ}$ C and after a reaction time of 2 h myrtanal (2) was achieved with 94% selectivity at almost complete conversion. With the Sn-Beta catalyst similar results were obtained with almost 90% selectivity at the same conversion level (Table 1, entry 2). A significantly lower conversion at the same reaction time was observed for Ti-Beta (Table 1, entry 3).

A comparison experiment using acetonitrile (2 h), nitromethane (30 min) or 1,4-dioxane (30 min) as solvent indicated that a competitive adsorption between acetonitrile and the reactant on the Lewis-acid center occurs. This is well in line with the Lewis-basic properties of acetonitrile, that make this molecule suitable to be used as probe molecule to study Lewis acidity [20]. On the other hand nitromethane and 1,4-dioxane are more weakly adsorbed on the Lewis-acid sites than acetonitrile.

With Sn-Beta in most solvents a lower product selectivity was observed with respect to the other two catalysts. The affinity of the tin center towards the carbonyl group of the product myrtanal (**2**) might be a possible explanation for this lower selectivity. In our previous theoretical calculations [3] for the interaction of the carbonyl bond of adsorbed cyclohexanone with the three different metals, i.e. Sn, Zr, and Ti, interaction is strongest for Sn-Beta. Hence, due to a longer adsorption time of the product on the Lewis-acid center in the case of Sn-Beta, the probability for further rearrangement reactions into structural isomers will be increased. When using acetonitrile as solvent, this can compete successfully with the carbonyl group of the myrtanal for adsorption, and facilitates product desorption, increasing thereof the selectivity from 70 to 89%.

The influence of solvent properties on product selectivity with the other two catalysts, i.e. Zr- and Ti-Beta, is not very pronounced. For Zr-Beta, the selectivities towards myrtanal (**2**) vary only within

Table 1

 $\beta$ -Pinene epoxide rearrangement in different solvents catalyzed by Zr-, Sn-, and Ti-Beta zeolite at 80 °C.

Entry	Catalyst	Solvent	Time [h]	Conv. [%]	Product s	electivity			Yield <b>2</b> [%]
					2 [%]	3 [%]	4 [%]	Other [%]	
1	Zr-Beta	Acetonitrile	2.0	98	94	2	1	3	92
2	Sn-Beta	Acetonitrile	2.0	98	89	2	2	7	87
3	Ti-Beta	Acetonitrile	2.0	74	86	2	2	10	64
4	Zr-Beta	Acetone <sup>a</sup>	2.0	98	77	2	11	10	75
5	Sn-Beta	Acetone <sup>a</sup>	2.0	90	70	4	13	13	63
6	Ti-Beta	Acetone <sup>a</sup>	2.0	99	84	2	8	6	83
7	Zr-Beta	Toluene	1.0	97	89	2	2	7	86
8	Sn-Beta	Toluene	1.0	>98	80	4	5	11	80
9	Ti-Beta	Toluene	1.0	87	89	2	2	7	77
10	Zr-Beta	Nitromethane	0.5	>98	87	2	3	8	87
11	Sn-Beta	Nitromethane	0.5	96	76	4	6	14	73
12	Ti-Beta	Nitromethane	0.5	>98	86	1	3	10	86
13	Zr-Beta	1,4-Dioxane	0.5	>98	90	2	3	5	90
14	Sn-Beta	1,4-Dioxane	0.5	97	82	2	6	10	80
15	Ti-Beta	1,4-Dioxane	0.5	98	87	1	3	9	85

<sup>a</sup> Reaction temperature 56 °C.

Table 2

 $Comparison of different metal-containing Beta zeolites as catalysts for the \beta-pinene epoxide rearrangement in acetonitrile as solvent after 2 h reaction time at 80 \,^\circ C.$ 

Entry	Catalyst	Si/M ratio [mol/mol]	Conv. [%] <sup>a</sup>	Product se	Product selectivity Y			
				2 [%]	3 [%]	4 [%]	Other [%]	
1	Zr-Beta	130	98	94	0	1	5	92
2	Sn-Beta	130	98	89	2	2	7	87
3	Ti-Beta	132	74 (84)	86	2	2	10	64
4	Nb-Beta	109	38 (41)	70	7	7	16	27
5	Ta-Beta	78	36 (40)	72	7	5	16	26
6	Al-Beta	103	46 (53)	74	8	5	13	34
7	Ga-Beta	45	37 (42)	63	9	6	22	23
8	Si-Beta	-	<5%					

<sup>a</sup> Values in parenthesis are the conversions after 4 h reaction time. Selectivities after 4 h are very close to those after 2 h.

#### Table 3

Recycling experiments for Zr-Beta zeolite as catalyst for the  $\beta$ -pinene epoxide rearrangement in acetonitrile as solvent. The catalyst was filtered out after each run of 2 h at 80 °C and re-activated by calcination (580 °C/3 h).

Entry	Cycle	Conv. [%] <sup>a</sup>	Product selectivity		Yield <b>2</b> [%]		
			2 [%]	3 [%]	4 [%]	Other [%]	
1	0	97	92	2	1	5	92
2	1	>98	94	2	1	3	94
3	2	>98	93	1	1	5	93
4	3	98	91	2	1	6	91
5	4	>98	93	1	1	6	93
6	5	>98	94	1	1	4	94
7	6	>98	94	2	1	3	94
8	7	>98	93	2	1	5	93
9	8	>98	93	2	1	4	93

a range of  $\pm$ 7% (except for acetone) reaching 94% with acetonitrile (cf. Table 1). The results for Ti-Beta were similar, with a selectivity range from 84% (acetone) to 89% (toluene).

Other metal-containing Beta zeolites were also tested using acetonitrile as solvent. Penta-valent metals such as niobium and tantalum, incorporated into the Beta framework by isomorphous substitution, show catalytic activity for the epoxide rearrangement reaction, although with moderate conversion and lower selectivity than before (cf. Table 2, entries 4 and 5). When Nb and Ta are incorporated into network positions of Beta zeolite, EXAFS and XANES spectroscopy indicate that the metal bears a M=O bond and is coordinated to three silyloxy framework groups [17].

Brönsted acidic zeolites such as Al-Beta and Ga-Beta gave conversions and selectivities considerably lower than Zr-Beta (cf. Table 2, entries 1, 6, and 7). Therefore, it can be concluded that Brönsted-acidic zeolites are not suitable catalysts for the present epoxide transformation. The incorporation of a metal is the origin of the catalytic activity since all silica Beta zeolite does not give considerable conversion under the studied reaction conditions (cf. Table 2, entry 8).

In summary, the epoxide rearrangement of  $\beta$ -pinene oxide into myrtanal occurred with highest selectivity (94%) at full conversion with Zr-Beta in acetonitrile as solvent. The Lewis-acid properties of Zr-Beta are the most adequate, providing high activity and effective desorption of the product. In the case of Sn centers, the stronger binding of the myrtanal product to the metal favours the occurrence of secondary rearrangements with the corresponding penalty on selectivity. With this last catalyst (Sn-Beta) best results are obtained when using acetonitrile as solvent, possibly due to the competitive adsorption of acetonitrile on the metal Lewis-acid site and a more efficient desorption of the desired product.

#### 3.3. Stability and recyclability of Zr-Beta

The reaction was carried out at a larger scale with Zr-Beta as catalyst and acetonitrile as solvent. The catalyst was filtered out after the reaction and re-activated by calcination in air at  $580 \degree C$  for 3 h. From the results in Table 3 it can be seen that even after nine reuses, conversion was practically complete after 2 h reaction time and selectivity remained high (approximately 95%) and constant, within the experimental error. Hence, in nine experiments 37.2 g of epoxide **1** were transformed with 0.500 g of Zr-Beta catalyst which corresponds to a turnover number (TON; defined as mol of reactant converted per mol of metal) of 3878.

After the nine cycles the recovered catalyst was characterized again and compared with the fresh catalyst. The X-ray diffraction pattern of the re-used sample was identical to the one of the fresh sample (cf. Table 4). SEM images of the fresh, calcined Zr-Beta catalyst and the same material after the 9 catalytic cycles were very similar and degradation of the zeolite crystals was not detected (cf. Fig. 4a and b, respectively). ICP analysis indicated the same Si/Zr ratio before and after the reactions.

#### Table 4

Analysis of fresh and used catalysts.

Catalyst	TON [mol/mol] <sup>a</sup>	Crystallinity [%] <sup>b</sup>	Si/Zr ratio [mol/mol] <sup>c</sup>
Fresh calcined Zr-Beta	-	100	131
Zr-Beta catalyst used in 9 cycles in a batch reactor	3878	100	129
Fresh calcined Zr-Beta-2	-	98	116
Zr-Beta-2 catalyst used in 6 cycles in a continuous-flow reactor	2130	100	113

<sup>a</sup> Mole of substrate converted per mol of metal sites (on an average).

 $^{\rm b}\,$  Compared with a commercial sample of Al-Beta; experimental error  $\pm\,5\%$ 

<sup>c</sup> Determined by ICP-OES.



Fig. 4. SEM images of Zr-Beta catalyst. (a) Fresh calcined Zr-Beta, (b) Zr-Beta catalyst after re-uses in batch mode, (c) fresh Zr-Beta-2 catalyst, and (d) Zr-Beta-2 after use in the fixed-bed continuous reactor.



Fig. 5. Epoxide rearrangement in the presence of Zr-Beta-2 in a fixed-bed continuous-flow reactor.

Taking all the above into account, it should be possible to use Zr-Beta catalyst in a fixed-bed continuous reactor. Hence, 800 mg of Zr-Beta-2 was placed in a tubular stainless-steel reactor and βpinene oxide dissolved in acetonitrile was passed at 80 °C. Again, excellent results were obtained for the conversion and selectivity of the  $\beta$ -pinene oxide rearrangement (cf. Fig. 5). The conversion was complete and the selectivity towards myrtanal (2) was 92%. After 80 min time on stream the conversion started to decrease and a short reactivation procedure was performed. To do that the reactor was heated to 500 °C and air (30 mL/min) was passed through for 20 min. Afterwards, the reaction was continued. By applying the reactivation procedure periodically, the catalyst could be used in several cycles at full conversion with a selectivity level of 92-96%. Thus 32.9 g of substrate were converted that corresponds to a TON of 2130 that certainly could be larger if the reaction was continued (cf. Table 4). Analysis of the used catalyst confirmed again the high stability of the catalyst. The used catalyst gave the same Xray diffraction pattern as the fresh one and SEM images show very similar crystal size and morphology for the fresh, calcined material and the reused catalyst (cf. Fig. 4c and d).

In previous work, we have seen that for Lewis-acid catalyzed reactions which present no diffusion constraints for reactants and products, Sn- or Zr-Beta are more active than the corresponding metal MCM-41 material. For the rearrangement of  $\beta$ -pinene oxide the results obtained here, under exactly the same reaction conditions (Table 1, entries 10–12; nitromethane solvent), as well as from the results obtained previously [10] we can say that M-Beta is also more active and selective than M-MCM-41 for production of myrtanal. This result confirms that there is no reaction control by diffusion for the rearrangement of  $\beta$ -pinene oxide to myrtanal with Beta zeolite, and this type of catalyst can be of interest for preparative chemistry as well as for industrial applications.

#### 4. Conclusions

Solid Lewis-acid sites in metal-containing Beta zeolite have been identified as active and selective for the epoxide rearrangement of  $\beta$ -pinene oxide to myrtanal. Among Zr-Beta, Sn-Beta, Ti-Beta, Ta-Beta, Nb-Beta, Al-Beta, and Ga-Beta, the former gives the best selectivity towards myrtanal (2) with yields up to 96% which is

much higher than any of the values previously reported in the patent and scientific literature. Materials involving Brönsted acid sites such as Al-Beta or Ga-Beta are much less suitable materials since they lack both activity and selectivity. For making better use of these solid Lewis-acid catalysts the solvent has to be selected to balance the competitive adsorption of the product. In this way, favouring product desorption is enhanced which results in a selectivity increase with only a small penalty on the rate of reaction.

Zr-Beta can be re-activated and used several times in a batch reactor or in a continuous-flow reactor achieving several thousands of TON (cycles per metal center; on an average). In conclusion, Zr-Beta is an active, selective and robust catalyst for the synthesis of myrtanal from  $\beta$ -pinene oxide, giving the highest yields reported up to now.

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