Catalysis Today xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Biomass to value added chemicals: Isomerisation of β-pinene oxide over supported ionic liquid catalysts (SILCAs) containing Lewis acids

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ARTICLE INFO

Article history:
Received 4 March 2014
Received in revised form 29 April 2014
Accepted 17 May 2014
Available online xxx

Keywords:
Isomerisation
Ionic liquids
SILCA

ABSTRACT

The isomerisation of β-pinene oxide was studied over supported ionic liquid catalysts (SILCAs) consisting of Lewis acids in immobilized ionic liquid. SILCAs were demonstrated as efficient catalysts for the transformation of β-pinene oxide to myrtanal with the product distribution and activity being dependent on the nature of the ionic liquid and Lewis acid strength of catalytic species. With the catalyst $ZnCl_2$/[N(3-OH-Pr)Py][NTf_2]/ACC, the highest myrtanal molar yield obtained was 68%.

1. Introduction

Environmentally friendly catalytic processes involving biomass valorisation to fine chemicals are an important topic which is continuously becoming more attractive in chemical engineering. Biomass derived terpenes, the main component of resins, and their oxides (e.g. β-pinene oxide) are important platform compounds for the pharmaceutical, speciality and fine chemical industry. β-Pinene oxide can be transformed to value added chemicals such as myrtanal, myrtenol and perillyl alcohol which have applications as fragrance and pharmaceutical chemicals [1]. Isomerisation of β-pinene oxide to myrtanal is promoted by Lewis acidic species while Brønsted acids give mainly perillyl alcohol and myrtenol (Fig. 1) [2–4].

Isomerisation of β-pinene oxide has been scarcely studied. Solid Lewis acid catalysts and homogeneous Lewis acids have been used in the isomerisation of β-pinene oxide. Metal modified Beta zeolites (e.g. Zr-Beta zeolite) are active and selective catalysts for the isomerisation of β-pinene oxide to myrtanal with yields varying from 64% to 92% [2]. With mesoporous molecular sieves such as Sn-MCM-41 and Ti-MCM-41, 64% and 49% selectivities towards myrtanal have been obtained at full conversions. Previously, tin modified Beta zeolites, Y-zeolites and Brønsted acidic resins have also been successfully applied in the isomerisation of β-pinene oxide to value added chemicals [3,4]. The use of heterogeneous catalysts in the isomerisation of β-pinene oxide is preferable because of the feasible catalyst regeneration and separation. Moreover, upon use of heterogeneous catalysts, accumulation of hazardous waste resulting from the use of corrosive mineral acids and homogeneous Lewis acids can be prevented.

Ionic liquids, also referred as room temperature molten salts, are ionic compounds in which either the cation or the anion (or both) is of organic origin. More simply, they are compounds built out of ions only. Ionic liquids generally display exceptional properties compared to conventional organic solvents such as tunable solvation properties, high thermal stability and low vapour pressure [5]. Nevertheless, the properties of ionic liquids cannot be generalized since many examples of species not fulfilling the aforementioned characteristics exist. Ionic liquids have many applications in heterogeneous catalysis. Optimally, ionic liquids can act as a catalyst and solvent at the same time [6,7]. In fact, immobilised ionic liquids can be catalysts themselves, as in the case of alkylation of benzene

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http://dx.doi.org/10.1016/j.cattod.2014.05.024
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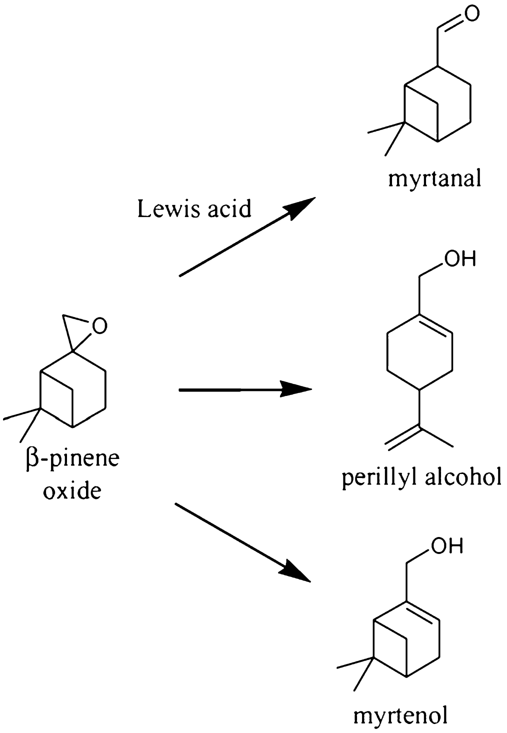

Fig. 1. β-Pinene oxide isomerisation reaction scheme.

over immobilised chloroaluminate ionic liquids [8]. Alternatively, ionic liquids can also act as a reaction environment as in the case of hydrogenation of citral where catalytic species such as palladium nanoparticles are residing in ionic liquid [9].

Concerning supported ionic liquid catalysts (SILCAs), the special properties of ionic liquids can be utilized by immobilizing them on solid support (e.g. active carbon cloth). SILCAs consist of catalytic species in a thin layer of immobilized ionic liquid (Fig. 2). The catalytically active species can be e.g. solid metal nanoparticles, enzymes or metal complexes dissolved in ionic liquids. One of the benefits of supported ionic liquid catalysts is the elimination of difficult and costly catalyst separation from the liquid reaction matrix [9]. Ionic liquids can be immobilized by means of grafting, sol–gel method, polymerization or simple impregnation which is the case with SILCA catalysts [9–12].

With the SILCA concept, some of the advantages of homogeneous and heterogeneous catalysis can be combined [13]. The ionic liquid can act as a reaction environment where the catalytic species are more active. Ionic liquids can also influence the concentrations of compounds and intermediates on the catalyst surface. Consequently, these characteristics of ionic liquids can lead to enhanced reaction rates [14]. As an example, ionic liquids have improved the rates and selectivities for many reactions such as hydrogenation of citral and cyclooctadiene [14,15].

The aim of this work was to synthesize, characterize and test different SILCAs containing Lewis acids in the isomerisation of β-pinene oxide. Various ionic liquids and Lewis acids were used for the catalyst preparation and these catalysts were tested for myrtanal production. SILCA catalysts were efficient catalysts for the isomerisation of β-pinene oxide to myrtanal.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared according to a simple impregnation method. Ionic liquid (150 mg) and Lewis acid (e.g. $ZnCl_2$, $SnCl_2$ or $CrCl_3$) were dissolved into suitable solvent (e.g. methanol or acetone). The mole fraction of metal chloride and ionic liquid was 2:1. The solution was poured over five pre-dried active carbon cloth (ACC) Kynol® pieces (approx. 1.5 g) followed by evaporation of the molecular solvent in an oven (80 °C) for two hours. As a result, Lewis acidic species in an immobilized ionic liquid was obtained. The ionic liquids used in the preparation of SILCAs were N-butyl-4-methylpyridinium tetrafluoroborate ([NB4MPy][BF_4], Merck, 98%), N-(3-hydroxypropyl)pyridinium bis(trifluoromethylsulfonyl)imide ([N(3-OH-Pr)Py][NTf_2], Merck, 98%), methyltrioctylammonium trifluoroacetate ([MO_3A][TFA], Merck, 98%) and N-butyl-3-methylpyridinium trifluoromethanesulfonate ([NB3MPy][OTf], Merck, 98%), stored under inert atmosphere and used without further purification.

2.2. Catalyst characterization

The surface area and micropore volume of the catalysts were characterised by means of automatic physisorption–chemisorption apparatus (Carlo-Erba instruments, sorptometer 1900). Dollim.–Heal method was used to calculate the micropore volume of the catalysts whereas the Dubinin method was used to calculate the surface area of the catalysts. The catalyst, 0.10 g of ACC, was outgassed for 3 h at 150 °C to eliminate the moisture. Nitrogen was absorbed and desorbed from the sample material which was subjected to −196 °C.

The spent catalyst was extracted with methanol to study the accumulation of different β-pinene oxide isomerisation products on the catalyst surface and the extractant solution was analysed by means of gas chromatography. The leaching behaviour of Lewis acidic metal species was studied by means of Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

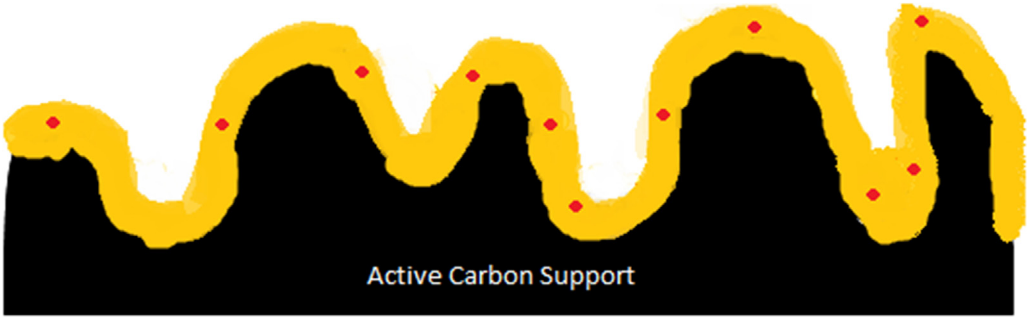

Fig. 2. Supported ionic liquid catalyst used in the β-pinene oxide isomerisation experiments.

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Table 1
Specific surface areas and micropore volumes of supported ionic liquid catalysts.

Catalyst	Surface area (m^2/g)[a]	Micropore volume (cm^3/g)[b]
Pure ACC	1720	0.67
$SnCl_2$/[N(3-OH-Pr)Py][NTf_2]/ACC	1402	0.49
$CrCl_3$/[N(3-OH-Pr)Py][NTf_2]/ACC	1314	0.46
$ZnCl_2$/[N(3-OH-Pr)Py][NTf_2]/ACC	1452	0.51
$ZnCl_2$/[NB4MPy][BF_4]/ACC	1270	0.45
$ZnCl_2$/[N(3-OH-Pr)Py][NTf_2]/ACC (spent)	915	0.32

[a] Calculated by Dubinin method.
[b] Calculated by Dollimore/Heal method.

2.3. β-Pinene oxide isomerisation

Isomerisation of β-pinene oxide was performed in a batch reactor (Parr Instrument Company, total volume 600 ml, liquid volume 250 ml) under argon atmosphere. High stirring rate (700 rpm) was applied to achieve the kinetic regime for the reaction. Approximately 0.46 g of (+)-β-pinene oxide (80+%, Advanced Technology & Industrial Company Ltd.), corresponding to a pure β-pinene oxide concentration of 0.0096 M, was dissolved in 250 ml of n-hexane (Merck, >99%) or toluene (Merck, >99%). Four pieces of active carbon cloth (1.2 g) containing ionic liquid and metal chloride (1:2 ratio of ionic liquid to metal chloride) were applied as a catalyst for the isomerisation experiment. The samples taken from the reactor were analysed by means of gas chromatography with a HP wax bonded polyethylene glycol column (30.0 m × 250 μm × 0.25 μm). In addition, a gas chromatograph coupled to a mass-spectrometer (Agilent 6980N GC with Agilent 5973 MS detector) was used to confirm correct identification of the products. The chemicals used for the product calibration were (1R)-(−)-myrtenol (95+%, Safc) and (S)-(−)-perillyl alcohol (90+%, Safc).

3. Results and discussion

3.1. Catalyst characterization

The results of nitrogen physisorption measurements of the selected catalysts are listed in Table 1. The specific surface area of pure ACC was found to be 1720 m^2/g and the micro-pore volume 0.67 cm^3/g, whereas the micropore volume of the catalyst $ZnCl_{2/}$[N(3-OH-Pr)Py][NTf_2]/ACC was 0.51 cm^3/g. The amount of ACC support used for a catalyst was approximately 1.5 g whereas the amount of ionic liquid was 150 mg. The densities of the ionic liquids [NB4MPy][BF_4] and [N(3-OH-Pr)Py][NTf_2], at ambient conditions, were 1.18 g/cm^3 and 1.55 g/cm^3, respectively [16]. Thus, it can be estimated that 10–20 vol% of the pore volumes were filled with an ionic liquid layer. Similar deductions can be made from the differences in surface areas and micro-pore volumes of pure ACC and fresh SILCAs. Specific surface area and micropore volume of the spent $ZnCl_{2/}$[N(3-OH-Pr)Py][NTf_2]/ACC was 915 m^2/g and 0.32 cm^3/g, respectively. Small specific surface areas and pore volumes of the spent catalyst indicated the accumulation of reaction compounds and organic impurities on the catalyst. This was further confirmed by extracting a catalyst with methanol and analysing the extractant by means of GC-analysis. The extractant from the spent catalyst revealed that small amounts of e.g. isomerisation products were agglomerated on the catalyst surface. Accumulation of reaction compounds and organic impurities is presumably one of the primary reasons for the catalyst deactivation as in the case of hydroformylation of propene with supported ionic liquid catalysts [17].

The leaching of metal species from the catalyst was studied by means of ICP-MS analysis. SILCAs containing zinc and tin chlorides were applied. Results from these leaching studies indicated that no leaching of metal species occurred during the experiments. Moreover, ionic liquids were not miscible with the bulk solvents (hexane and toluene) used.

3.2. β-Pinene oxide isomerisation

Results from β-pinene oxide isomerisation experiments with different SILCAs are compared in Table 2. Four different ionic liquids were tested for β-pinene oxide isomerisation. The effect of ionic liquid to myrtanal selectivity was studied over SILCAs containing tin chloride ($SnCl_2$) as a Lewis acid. [N(3-OH-Pr)Py][NTf_2] and [NB4MPy][BF_4] were the most efficient ionic liquids for the myrtanal production (Table 2, entry 1–2). It can be observed that ionic liquids have an effect to the product distribution. The reason for this behaviour is that ionic liquids influence to the concentrations of products and intermediates on the surface of the catalyst [14].

On the other hand, zinc chloride ($ZnCl_2$) was the most efficient Lewis acid catalyst when aiming at myrtanal production. Three different Lewis acids were applied with the ionic liquid [N(3-OH-Pr)Py][NTf_2]. The zinc chloride modified SILCA resulted in 54% molar yield of myrtanal (Table 2, entry 6).

β-Pinene oxide isomerisation experiments were performed at temperature range of 25–120 °C applying $ZnCl_2$/[N(3-OH-Pr)Py][NTf_2]/ACC and $ZnCl_2$/[NB4MPy][BF_4]/ACC catalysts. The effect of temperature in the isomerisation of β-pinene oxide over $ZnCl_2$/[N(3-OH-Pr)Py][NTf_2]/ACC and $ZnCl_2$/[NB4MPy][BF_4]/ACC catalysts are illustrated in Figs. 3 and 4, respectively. The reaction rates were higher at higher temperatures as expected. The highest molar yields of myrtanal, obtained with the catalysts $ZnCl_2$/[N(3-OH-Pr)Py][NTf_2]/ACC and

Table 2
Molar yields of products from β-pinene oxide isomerisation reactions (after 4 hours). Reaction conditions were $T = 70\,^{\circ}C$, p(Ar) = 5 bar and $V_{hexane} = 250$ ml. IL_1 = [N(3-OH-Pr)Py][NTf_2], IL_2 = [NB4MPy][BF_4], IL_3 = [MO_3A][TFA] and IL_4 = [NB3MPy][OTf].

Entry	Catalyst	Conversion [%]	Myrtanal [%]	Perillyl alcohol [%]	Myrtenol [%]	Other products [%]
1	$SnCl_2/IL_1$/ACC	100	38	16	8	38
2	$SnCl_2/IL_2$/ACC	100	41	15	9	35
3	$SnCl_2/IL_3$/ACC	80	38	10	11	21
4	$SnCl_2/IL_4$/ACC	68	25	13	7	23
5	$CrCl_3/IL_1$/ACC	100	28	25	15	32
6	$ZnCl_2/IL_1$/ACC	100	54	15	4	27
7	$ZnCl_2/IL_2$/ACC	100	50	12	4	34
8[a]	$ZnCl_2/IL_2$/ACC	100	52	12	0	36
9[b]	$ZnCl_2/IL_1$/ACC	100	68	18	6	8
10[b]	$ZnCl_2/IL_2$/ACC	100	65	11	4	20

[a] Toluene as a solvent.
[b] Reaction conditions were $T = 120\,^{\circ}C$ and p(Ar) = 5. Product yields are illustrated after total conversion.

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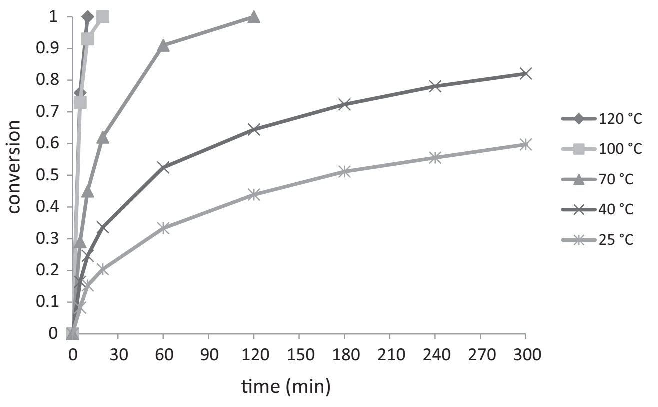

Fig. 3. Effect of temperature in the isomerization of β-pinene oxide over $ZnCl_2$/[N(3-OH-Pr)Py][NTf_2]/ACC catalyst. Reaction conditions were p(Ar) = 5 bar and V_{hexane} = 250 ml.

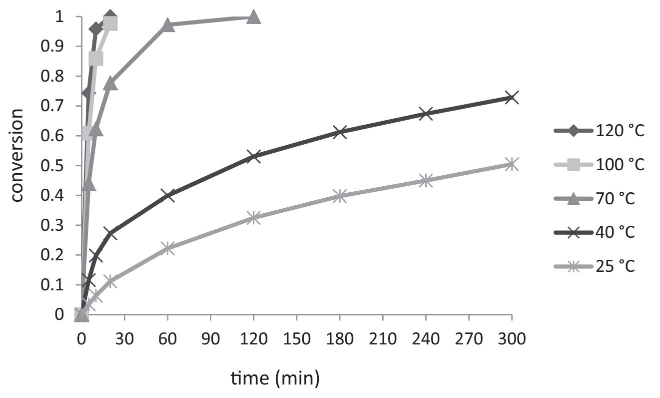

Fig. 4. Effect of temperature in the isomerisation of β-pinene oxide over $ZnCl_2$/[NB4MPy][BF_4]/ACC catalyst. Reaction conditions were p(Ar) = 5 bar and V_{hexane} = 250 ml.

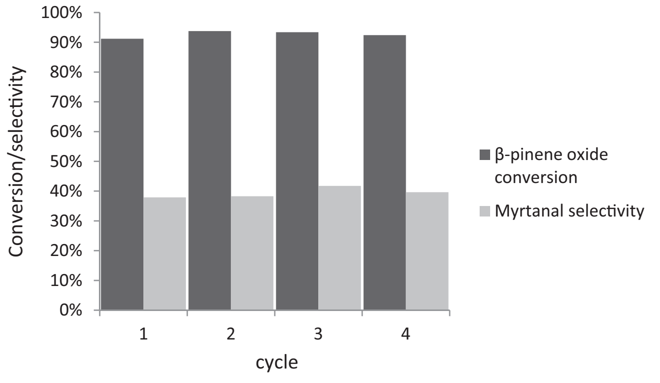

Fig. 5. Deactivation of the catalyst containing $SnCl_2$/[N(3-OH-Pr)Py][NTf_2] (2:1 molar ratio) on ACC during four consecutive β-pinene oxide isomerisation experiments after 3 h. The reaction conditions were T = 70 °C, p(Ar) = 5 bar and V_{hexane} = 250 ml.

$ZnCl_2$/[NB4MPy][BF_4]/ACC at 120 °C, were 68% and 65%. At lower temperatures, the molar yields of myrtanal were lower. With the higher reaction temperatures, the selectivity to myrtanal increased. This phenomenon has also been observed for Sn-modified zeolites at a temperature range of 27–70 °C [4]. On the basis of these results it can be deducted that short reaction times and high temperatures favour the formation of myrtanal.

SILCA catalysts (Table 2, entry 1) were recycled in four consecutive β-pinene oxide isomerisation experiments in order to study the catalyst deactivation. It turned out that the catalyst could be very well reused four times (Fig. 5). Moreover, the product distribution was not altered during the deactivation study. One of the main reasons for the catalyst deactivation is the accumulation of β-pinene oxide isomerisation products into the ionic liquid layer as in the case of hydrogenation of citral and hydroformylation of propene with supported ionic liquid catalysts [15,17].

4. Conclusions

β-Pinene oxide isomerisation to myrtanal could be successfully carried out applying heterogenised Lewis acidic species in SILCAs. SILCAs are efficient and durable catalysts for the transformation of β-pinene oxide into myrtanal with the product distribution and activity being dependent on the nature of the ionic liquid. It was concluded that short reaction times and high temperatures favour the formation of myrtanal. With the $ZnCl_2$/[N(3-OH-Pr)Py][NTf_2]/ACC catalyst at high temperatures, 68% molar yield of myrtanal was obtained.

Acknowledgements

This work is part of the activities at the Åbo Akademi Process Chemistry Centre, a centre of excellence financed by the Åbo Akademi University. The Academy of Finland is gratefully acknowledged for financial support. In Sweden, the Bio4Energy programme, Kempe Foundations and Wallenberg Wood Science Center under auspices of Knut and Alice Wallenberg Foundation are acknowledged. The Cost actions CM0903 (UbioChem) and CM1206 (EXIL) are also acknowledged.

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