REVIEW ARTICLE

A REVIEW ON CATALYTIC TERPENE TRANSFORMATION OVER HETEROGENEOUS CATALYST

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Abstract

Heterogeneous catalysis and their application in industrial-scale organic synthesis of fine chemicals are greatly facilitated by catalysis and further on by catalyst recovery and recycles to fits most "principles of green chemistry. In acid media, terpenoids generally undergoes various transformations. The terpenoid transformations include various liquid Bronsted and Lewis Acids, Acid clays, Hetropoly acids, Zeolites, Ion- exchange resins etc.Montmorillonite clays were generally the most popular catalyst of pinenes isomerisation. The heterogeneous catalysis by $H_3PW_{12}O_{40}$ (hetropoly acid) exhibit higher catalytic activity in various reactions of terpenoids such as hydration, acetoxylation, and isomerisation.Metalloporphyrins, the porphyrin complexes are efficient catalyst in the oxygenation of terpenes. Zeolite played a role in heterogeneous catalysis. Cobalt containing MCM-41 Zeolite Catalyst was used as a heterogeneous catalyst for the liquid-phase aerobic oxidation of isolongifoline. The synthesis of nopyl with strong acidic cation exchange resin Amberlyst 15 and the ion exchange of isolongifoline from longifoline were carried out by using macroporous strong acid type cationic exchange resin as catalyst.
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Keywords: Heterogeneous catalyst, Acidic clays, Zeolites, Hetropoly acid, Ion exchange Resin.

1. Introduction

Monoterpenes, sesquiterpenes and their derivatives have great value in fragrance and perfumery and may be acyclic, monocyclic, bicyclic and tricyclic. Terpenes and their derivatives are valuable raw material in organic chemistry for preparation of products of desired odour value useful in perfume and pharmaceuticals. Terpenes and their derivatives are valuable raw material in organic chemistry. Their unique structure is often combined with high chemical labiality and optical activity. Many terpenoids have been used in the pharmaceutical and cosmetics industries, production of flavour additives. [1, 2]

Suitable catalyst provides a solution to make it possible for the reactions to proceed at rates high enough to permit their commercial exploitation on large scale, with resulting economic benefits for everyone [3]

To date, catalytic technologies leading to fine chemicals production, and particularly in selective ,large scale processes, are still largely dominated by homogeneous catalysts, [4,5,6,7,8,9,10], Whose separation from the reaction products and reuse is a major concern.[11,12]

A variety of solid, often highly sophisticated, have been exploited for this purpose, including inorganic (Silicaclays, Zeolites, metaloxide, hetropolyacidsetc) [13, 14, and 15]. The active species can be immobilized on this support by covalent or non covalent binding, i.e. by adsorption, electrostatic interaction, or entrapment [16, 17].

Estimates are that 90% of all commercially produced chemical products involve catalysts at some stage in the process of their manufacture [18]. Now days, the chemical industry is under increased pressure to develop cleaner production processes and technologies. Much effort is devoted to development of heterogeneous catalysis, their application in industrial-scale organic synthesis of fine chemicals and abatement of pollutants that are determined to environment [19, 20]. Chemical synthesis is greatly facilitated by catalysis and further on by catalyst recovery and recycles. Catalyst reuse increases the overall productivity and cost effectiveness of chemical transformations while minimizing their environmental impact, ultimately contributing considerably to the sustainability of chemical processes. Indeed catalyst recycle fits most "principles of green chemistry" [21, 22, 23, 24] the technologically important reactions of terpenes are of six main types− [25]

1. Acid-catalyzed rearrangement, additions, and eliminations
2. Thermal rearrangements
3. Allylic rearrangements
4. Hydrogenations and other reductions, and dehydrogenations
5. Stereochemical changes (epimerization)
6. Oxidations, including halogenations

Synthesis of fine and specialty chemicals involving heterogeneous catalyst according to the type of reactions, Catalytic terpene transformations over heterogeneous catalysts have been recently summarized [26, 27, 28, 29]. Most of the recent catalytic literature presents acid catalyzed isomerisation of terpenes over different catalyst [30, 31, and 32]. Oxidations and epoxidation of terpenes [33, 34, 35] hydrogenation, dehydrogenation, [36, 37] estrification etc. [38, 39]

2. Cataltic terpene transformations over hetrogeneous catalyst

2.1. Acidic Clays as Catalyst in Synthesis of terpene derivates

Using clays as catalysts of terpenoids transformations leads to improved characteristics of known process and often to reaction routes other than those that occur in presence of traditional acid catalysts. This opens up new prospects for the application of renewable plant raw material in fine organic chemistry. [40]

In acid media, terpenoids generally undergoes various transformations. The complex mixtures of products obtained in these transformations are the major factors that hinder the wide use of these compound in fine organic chemistry. However due to significant dependence of the products ratio on the type and characteristics of the acid catalyst used, one can occasionally select favourable conditions for the synthesis of desired product, which stimulate the search for new catalytic systems and reaction conditions. [41, 42]

The acid catalysts of the terpenoid transformations include various liquid Bronsted and Lewis Acids, Ion- exchange resins, Zeolites, etc. These are inexpensive and accessible catalysts that often lead to new routes of terpenoids transformations or give other products ratio than other acid catalysts. The use of clays as catalyst of terpenoids transformations has not received due attention, although a number of publications reviewed their use for catalyzing various organic reactions. [43, 44, 45, 46, 47]

Montmorillonite clays were generally the most popular catalyst of pinenes isomerisation, although kaolinitic clay was also successfully used for this purpose. [48] Preliminary acid treatment of clays had a considerable effect on the conversion of pinenes and the product ratio [49] the amount of acid used [50, 51] and, its concentration [52, 53] and the temperature of acid treatment [54] were reported to be more important factor in this case. The data about the dependence of the catalytic activity of acidic clays and isomerisation selectivity on the nature of acid ceteres, obtained in these works indicated that the transformations of pinenes in to camphene occurred predominantly on the Bronsted acid centers. [55, 56] Figure 2.10 shows the isomerisation of alpha pinene.
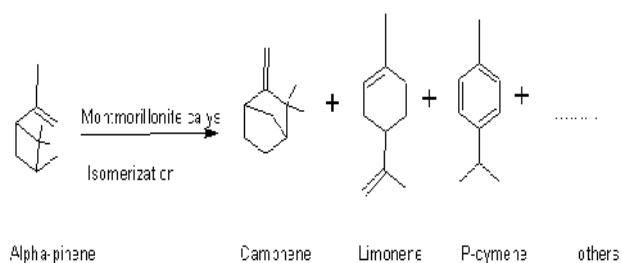

Figure 2.10: Isomerisation of Alpha –pinene in Monmorillonite clays

Studies of the effects of the exchange cation on the isomerizationof   -pinene showed that

montmorillonite clays containing the Fe3+ cation exhibited the highest activity. Isomerization of - pinene in the presence of acid-treated polycationexchanged montmorillonite clay led to a considerably increased yield of camphene compared with the yield obtained in the presence of the non-polycation-exchanged equivalents [57] Investigation of the applicability of montmorillonite clays containing organic cations (tetramethylammonium, dodecyltrimethylammonium and octadecyltrimethylammonium) as exchange cations to isomerisation of -pinene revealed that only organoclays pre-treated with an acid possessed high catalytic activity [58,59] The Al3+ exchange cations used in combination with tetramethylammonium proved less effective in isomerisation of -pinene than Al3+-exchange clays because conversion decreased substantially when the tetramethylammonium content increased [60] Alumina pillared clays demonstrated [61] good activity and high selectivity with respect to camphene .The selectivity of the best catalysts based on clays in isomerisation of -pinene generally was 40-65% with respect to camphene and 15-40% with respect to limonene , while conversion of -pinene was 70-90%..

Isolongifolne and various other isolongifoline-based products are commercially important chemicals that find application in perfumery and fragrance industries.Isomerization of longifoline to Isolongifoline (Fig.2.11) in the presence of calys-montmorillonite, pillared clay and modified pillared clay was studies. [62] As analysis of the results confirmed that the total strength along with the acid site distribution played a vital role in selective isomerisation of longifoline to Isolongifoline .catalyst with a very low and very high total acidity with large numbers of weak acid site were not suitable for this isomerization because side reaction dominated the reaction pathway. The use of Al- and Zr-pillared clays at 180^0C yielded reaction mixture with more than 70 % Isolongifoline.

The isomerization of longifolene [63] using montmorillonite clay K10 as catalyst at 120° C (Fig. 2.11) with 100% selectivity and more than 90% conversion. However the process has drawback in using natural clays which have lot of impurities and difficult to reproduce with the requisite surface acidity. Furthermore, the thermal stability of the clays of the clays is low and these get deactivated with use and regeneration and re-usability of the clay catalyst is not known.
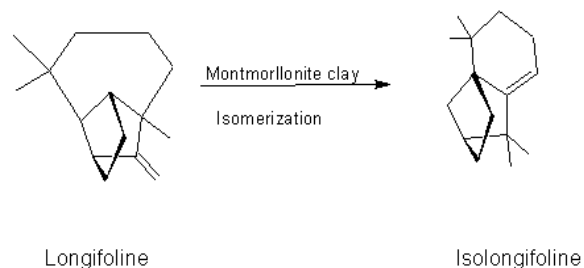

Figure.2.11: Isomerization of Longifoline in Montmorllonite Clays

For terpenes isomerized on clays, the major effect on the product ratio is exerted by nature and strength of acid sites, while for oxygen containing terpenes, other characteristics of clay as catalyst are also very important, namely, three-dimensional crystal structure, the mutual arrangement of active centers, etc.As a result, unlike the case with the traditional acid catalyst, the presence of clays favours activation of particular functional groups and particular terpenoid conformations can be fixed in the course of adsorption, and these factors can determine the direction and stereo selectivity of transformations.

The reaction of –pinene and -Pinene with acetic anhydride on clay K-10 gave not only products (a) and (b) (Fig. 2.12) formed as results of the isomerization of pinane framework to the p-menthane and bornane frameworks, respectively but also compound (c) which resulted from from a more profound rearrangement of the pinene framework [64] Although both pinenes were expected to give the same cation after protonation, the composition of the reaction mixture dependent on the structure of the starting pinene; the ratio of products (a) (b) and (c) in the reaction mixture was 2.5 : 3 : 1 in the case of –pinene and 4 : 2 : 1 in the case of pinene.
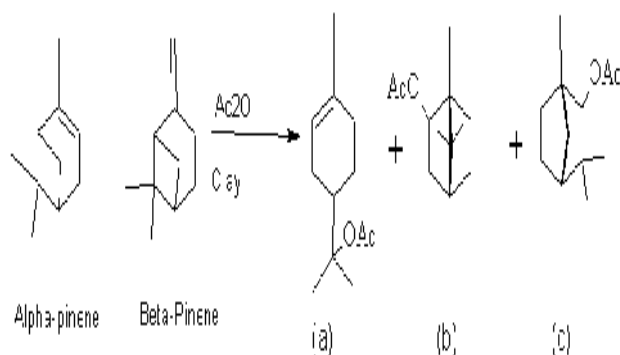

Figure.2.12. Reactions of Pinenes with acetic anhydride on clay

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Clay may catalyze chemical reactions by acting as Bronsted acids, Lewis acids, and/or Lewis bases. The changes occurring when limonene (p-menthadiene) is heated in presence of montmorillonite illustrate how Bronsted and Lewis acidity may operate competitively, the nature of interlayer cations determining which reactions dominates. The rate at which the starting material disappears increases with the acidity of the clay, which depends upon the interlayer cations (Na < Mg< Al<H) The concentration of disproportionation and isomerization products reaches a maximum after reaction times which decrease with increasing surface activity of the clay. P-cymene is produced by oxidation in concentrations inversely related to the surface acidity of the clays. The course of chemical reaction can thus be steered in the preferred direction by an appropriate choice of interlayer cations. [65]

Using Clays for acid-catalyzed transformations proved a fruitful approach. Apart from the traditional advantages of heterogeneous acid catalysis such as no acid wastes, facile treatment of reaction mixture, catalyst regeneration and recycling, etc.The transformations of terpenoids in the presence of clays are generally streoselective processes. The information's about these transformations obtained during the last decade allow us to pass from the reactivity studies of terpenoids on clays to practical application of products.

2.3.2 Hetropoly Acids as Catalysts for synthesis of Terpenes

Hetropoly acids (HPAs) have attracted interest as catalyst for clean synthesis of fine and specially chemicals. [66] Due to their strong acidity, HPAs generally exhibit higher catalytic activity in various reactions of terpenoids such as hydration, acetoxylation, and isomerisation [67, 68, 69] in homogeneous and heterogeneous catalysis by $H_3PW_{12}O_{40}$ (PW), the strongest HPA in the Keggin series.

Silica supported PW (20wt %) is an efficient heterogeneous catalyst for the liquid-phase isomerization of various compound such as -pinene, - pinene oxide, longifoline and -terpineol, in to more valuable isomers. For example, - pinene and longifoline can be converted in to camphene and isolongifoline, respectively. (Fig.2.13)Which are intermediate in the synthesis of valuable fragrances? These two reactions occur under solvent free conditions in temperature range 80 – 100 ^{0}C, with low catalyst loading (0.15 – 5 wt %). [70]
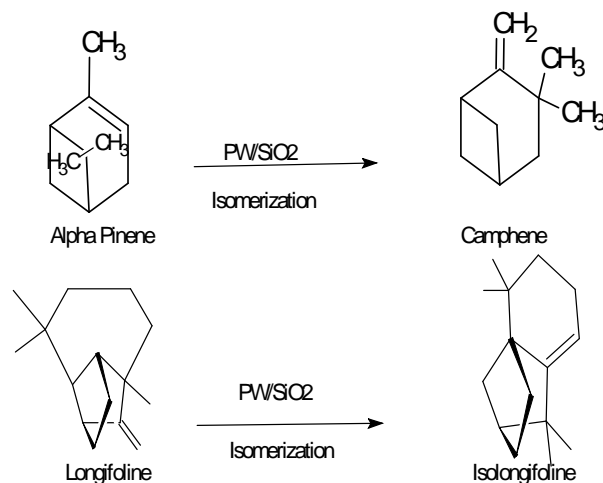

Figure.2.13. Isomerization of Alpha Pinenes and Isolongifoline on Hetropoly acid

The isomerization reaction in liquid phase of -Pinene in camphene catalyzed by tungstophospheric acid supported on silica ($H_3PW_{12}O_{40}/SiO_2$) is studied. The catalyst is catalyzed with FT-IR and XRD to establish if the tungestophosphoric acid maintains the keggin structure after being supported. The catalyst acidity exposed to different thermal treatment was determined by using FT-IR and TPD technique of ammonia adsorbed. Two types of sites are distinguished, weak acid sites and strong acid sites. The weak acid site concentration increases with the thermal treatment and can be responsible for the selectivity decreases in camphene by formation of products of higher molecular weight, while the strong acid sites concentration remains almost constant affecting in a lesser degree the abstention of monocyclic compounds. [71]

The isomerization of - terpineol (Fig.2.14) catalyzed by hetropoly acid ($H_3PW_{12}O_{40}$) in homogeneous and heterogeneous system yields yields 1, 8-cineole and 1, 4-cineole in good yield. Both are useful for flavoring and pharmaceutical applications. In homogeneous system 1,8 cineole and 1,4 cineole obtained with 25 % and 23 -27 % selectivity, respectively at 50 -90 %   - terpineol conversion (in a nitrobenzene solution, 40 ^{0} C) In heterogeneous system,35% of 1,8 cineole and 25 % of 1,4 cineole were obtained at 70 – 100 % conversion in cyclohexane solution at 60 ^{0} C using silica supported PW as a solid catalyst, and the catalyst could be recycled PW showed a higher catalytic activity and selectivity than conventional acid catalyst such as H_2SO_4 and Amberyst-15. [72]
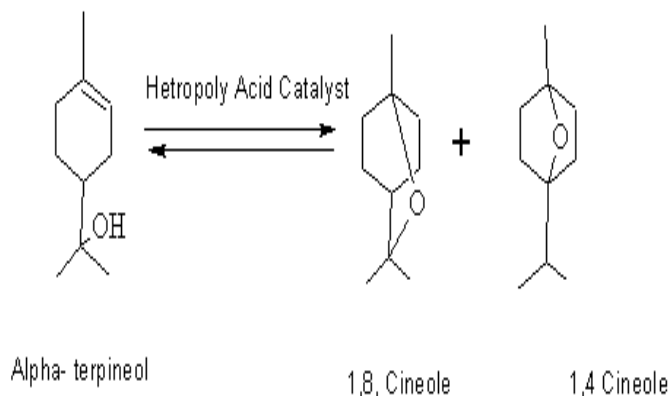
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Figure.2.14: Isomerization of Alpha- Terpineol on Hetropoly Acid Catalyst

Epoxidation of isolated and allylic olefins with doceca-phosphotungestic acid ($H_3PW_{12}O_{40}XH_2O$) and Urea Hydrogen peroxide (UHP) adduct an oxidant has successfully been carried out under homogeneous conditions with the aid of isopropanol : water (4 :1) as solvent, thereby avoiding the use of expensive phase transfer catalyst, Synthesis of several acid labile epoxide ranging from monoterpenes to sesquiterpenes lactones are carried out by using UHP in combination of doceca-phosphotungestic acid ($H_3PW_{12}O_{40}XH_2O$). [73]

The oxidation of terpenes is an importent industrial application as their epoxide are used as starting materials in the synthesis of commercially important fragrance and flavour materials. Literature reveals growth regulating property

2.3.3 Metalloporphyrins and metallic as catalysts in the oxidation of terpenes

Terpenes are an abundant group of natural compounds that can be transferred into products of higher commercial value. One of the approaches for the functionalization of terpenes is the oxidation in the presence of an oxygen donar, under the influence of a suitable catalyst.Metalloporphyrins, with structure based on the well known meso-tetraphenylporphyrin (TPPPH$_2$), are amongst the catalyst commonly studied. The porphyrin complexes have demonstrated to be efficient catalyst in the oxygenation of terpenes; these transformations have been studied in the presence of different oxygen atoms donors oxidations under heterogeneous conditions have been demonstrated certain advantages when compared with those carried out homogenous phases, but the catalyst availability needs to be overcome. [74]

An important trend for all kinds of oxidations reactions is the use of environmentally more benign oxidants and catalyst. The choice of the respective oxidants determines to a large extent the practicability and efficiency of the respective reaction. Clearly the use of stoichiometric metal oxide should be avoided. Among the different oxidants, air with its oxygen is an ideal reagent for oxidation reactions. However the use of air or pure O_2 is of difficult control and dangerous combustions might come up; also those processes taking place with O_2 have 50 % atom efficiency. In addition to molecular oxygen, hydrogen peroxide (H_2O_2) is a cheap, waste-avoiding oxidant. It can oxidize organic compounds with an atom efficiency of 47 % and (theoretically) generates only water as co-product. Due to its properties, H_2O_2 is particularly useful for liquid-phase oxidations used for the synthesis of fine chemicals. However, there exists a recent trend to use these oxidants also for bulky processes. [75]

Meunier and collaborators described a comparative study involving four magnesium (III) porphyrins in the oxidation of -pinene and –terpinene, at ambient temperature, using NaClO or KHSO$_5$ as oxidants, 4-butylpyridine as co-catalyst and benzyldimethyltetradecyl-ammonium chloride as the phase transfer agent; the reaction were in two phase system, with CH_2Cl_2 as the substrate solvent and the oxidant in the aqueous phase. In the presence of an excess of NaClO, the conversion of –pinene always greater than 97% and the distributions of products was dependent on the porphyrin ring substituents. The best yield for the –pinene oxide was obtained with less hindered ring porphyrin, Mn (TPP) Cl. [76]

The Authors have enhanced the fact that when the stereo hindrance due to substitution in the aromatic porphyrin rings increases, the epoxide yield diminishes, increasing the amount of allylic oxidation products. The authors have suggested that the electronic properties of the substituents in the aromatic rings of the porphyrin complexes must be considered along with the stereochemical factors. That is the case of Mn (TDCPP)Cl, a compound with two chlorine atoms (which are moderately electron-withdrawing substituent's) in 2,6-positions of the phenyl group, in contrast to Mn(TNPP)Cl, with one p-nitro substituent's in each phenyl group (case of strong electron-withdrawing effect).In the first case, trans-verbenol is formed in 29 % yield, without traces of verbenone, while with Mn(TNPP)Cl the verbenone is formed in 16 % yield, without traces of verbenol (Fig. 2.15). [76]
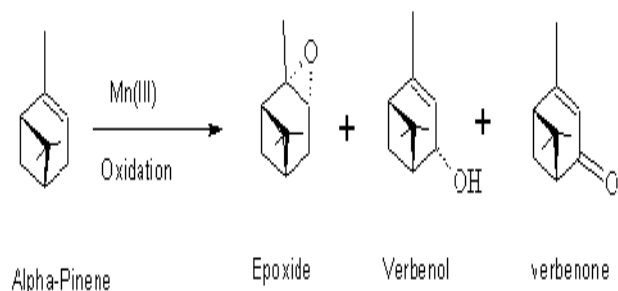
Figure.2.15. Oxidation of Alpha- Pinenes with Metallopophyrins Catalyst

When $KHSO_5$ was used as oxidant, without a co-catalyst, the authors verified that the selectivity was usually lower and other products beyond the epoxide, verbenol and verbenone were formed, except with Mn (TDCPP) Cl, when the epoxide was formed 96% yield with 100% substrate conversion. When a co-catalyst was used with $KHSO_5$, the results have been similar to those obtained with NaClO. [76]

The use of heterogeneous catalyst offers advantage (like easier recovery, recycling and increased stability) when compared with those in homogeneous conditions. A polystyrene –supported tetra (4-pyridyl) porphyrinato manganese's (III) was found to be to be efficient catalyst for the (R)-(+)-limonene epoxidation by sodium periodate, among several other alkenes. The epoxidation of (R)-(+)-limonene (92% of conversion after 3 hrs of reaction) afforded mainly the 1,2-epoxide (55% yield) against 37% yield for the 8,9-epoxide.Under the conditions used, this heterogenized metalloporphyrin catalyst showed high stability and reusability. [77]

2.3.4 Zeolite as heterogeneous Catalyst for synthesis of Terpenes derivatives

Zeolite has been playing a role in heterogeneous catalysis. An impressive number of large –scale industrial processes in petroleum refining ,petrochemical and the manufacturer of organic chemicals are carried out using zeolite catalyts.Altogether ,zeolite catalysis has become a most important sub-filed of heterogeneous catalysis. [78] Zeolite occur in nature and have been known for almost 250 years as aluminosilicate minerals , Approximate 40 natural zeolite have identified the most common of which are analcime, chabazite, clinoptilolite,ferrierite, heulandites, mordenite and phillipsite.Today , Zeolite structure are of great interest in catalysis. Synthetic zeolite has been encountering a growing interest of their application as catalysis in industry. Some of more common synthetic zeolite are Zeolite A, X, Y, ,

ZMS-5, MCM-41 and Mordenite. Natural and synthetic Zeolites are used commercially because of their unique adsorption, ion exchange and molecular sieve properties as catalyst .Zeolite research covers an even wider area, including catalytic and ion exchange properties of Zeolites, Zeolite synthesis and the behavior of molecules adsorbed on the Zeolite surface. [79, 80] Most important sources of terpenes are the turpentine and essential oils. Within this group of compounds, -Pinene, camphene, limonene and P- cymene are major importance for chemical and pharmaceutical industry. All of these molecules can be obtain by the catalytic isomerization of -Pinene. The acid-impregnated TiO_2 is currently used as an industrial catalyst for this purpose, but because of the low rate of the process, there is a great interest in finding new catalysts exhibiting higher activity and higher selectivity to camphene and/or limonene. Zeolites catalyze a large number of reactions, due to their strong acidity and shape selectivity. The Zeolites -ZSM-5(MFI),ZSM-12(MTW) and MCM-22(MWW), representing three different structure types, were chosen for studies of the -Pinene isomerization.ZSM-5,ZSM-12 and MCM-22 zeolites exhibit different behaviour in the isomerization of -Pinene. The highest conversion was observed for MTW type material with the Si/Al=40.The conversion level depends both on the alumina content and reaction temperature. [81]

Cobalt containing MCM-41 Zeolite Catalyst was used as a heterogeneous catalyst for the liquid-phase aerobic oxidation of isolongifoline, one of the most available sesquiterpenes. The Oxidation of isolongifoline (Fig.2.16) under mild solvent-free condition results 90% selectivity in isolongifoline -9-one, a compound which occupies a vintage place in modern perfume industry. The total concentration of oxygenated products in the final mixtures reaches 90wt%.A silica-included cobalt catalyst prepared through a conventional sol-gel method shows a catalytic activity comparable with that of Co-MCM-41; however selectivity is much lower. [82]
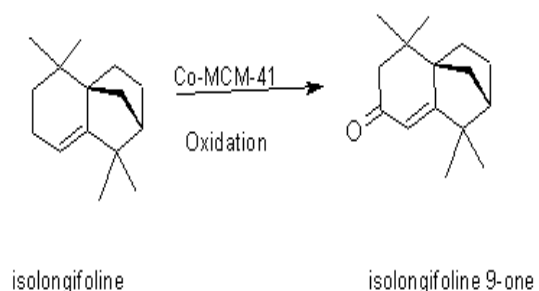

Figure.2.16. Oxidation of isolongifoline by Co-MCM-41 Zeolite Catalyst

2.3.5 Ion Exchange Resin as Catalyst in synthesis of terpene derivative

Polystyrene supported sulfonic acid resins are widely used as acid catalysts in many kinds of petrochemical reactions, such as production of ethers, alkene hydration, esterification and other reactions. Organic esters attract more attention, which are widely used in the manufacturing of perfumery, flavours, pharmaceuticals, plasticizers, polymerization monomers, emulsifiers in the food and intermediates.

The uses of ion-exchange resins as catalysts or catalyst precursors in organic synthesis, for the preparation of fine or intermediate chemicals. Twelve families of reaction have been covered and presented according to the molecules to be synthesized, regardless of the anionic or cationic nature of the resins; 300 references have been selected from January 1980. In acid-catalyzed reactions, the contribution of both Lewis acidity and Brönsted acidity are mentioned, and, when available, some aspects related to the stability or the recycling of the catalysts is reported. In base-catalyzed reactions, the importance of the thermal stability of anionic resins has been underlined." [83]The use of ion exchange resin catalysis has led to an improvement in the selectivity of the desired products. [84] Cations are located in the Resin framework, mobile and occupy various exchange sites depending upon their radius, charge, and degree of hydration, The cation exchange behaviour of Ion Exchange depend upon: The nature of the cation species, temperature, the concentration of the cation species in solution, the anion species associated with cation in solution, the solvent, The structural characteristic of the particular Resin.

Camphene is an industrial intermediate compound for commercial chemicals chemicals such as isoborneol, isobornyl acetate and camphor. Industrially, the conventional process for camphene production consists of the isomerization of -pinene using acidic TiO2 as catalyst. The use of this catalyst presents problems such as considerable time for preparation, reproducibility and recovery of catalyst from products after the -pinene isomerization, For the first time, a commercial exchange resin was used for this reaction, based on the concentration of product as a function of the reaction time, the path of -pinene transformation to camphene and by-products is proposed. Temperature and alpha-pinene and catalyst ratio were studied in order to optimize the yield to camphene production. The obtained results were comparable with those reported for acidic TiO2. [85] Terpene- catechol was synthesized with turpentine oil and catechol as raw material, strong acidic ion exchange resins as catalyst. The condition of the reaction was discussed; the structure of the product was analyzed by UV and IR. And average molecular weight was measured. The result showed that terpene –catechol was synthesized by alkylation reaction of catechol and terpentine, the catalyst could be reused many times, and the product was easily separated; the optimum reaction conditions were as follows ,it had reached for 16 hrs, temperature was 120 0c., the molar ratio of terpentine ratio was 3:1, the amount of catalyst was 10%.[86]

In a process for preparing terpene esters by reaction of camphene and a low molecular weight carboxylic acid over an acid exchanger as catalyst, the reactant are passed from below through the acid ion exchanger located in a column-shaped reactor at such a velocity that the ion exchange is suspended to uniformity fill the reactor, that is gives a pseudofluid suspended bed. In the case of preparation of isobornyl acetate, high specific catalyst productivity, a high selectivity of the reaction with formation of small amount of other esters, a high degree of conversion of the reaction component used in substoichiometric amount and high total catalyst productivity are achieved. [87]

Kinetics study of the direct hydration of turpentine was carried out, using macropore and strong acidic cation exchange resin Amberlyst 15 wet as catalyst. During the hydration process, the isomerization of - pinene also took place under the catalytic condition. The effect of different parameter such as agitation speed, catalyst type, catalyst loading, mass ratio of reactant, temperature and reusability of the catalyst on the conversion of turpentine and yield of - terpineol were investigated in a stirred-tank reactor. Based on these optimized conditions the investigation was conducted in a new pilot – scale jet reactor to achieve excellent performance. The kinetics of the direct hydration reaction was also performed in the temperature 325.15 – 348.15 K. A pseudo homogeneous (pH) model was used to explain the reaction rate equation and to determine the reaction rate constant and reaction activation energy. [88]

Synthesis of nopyl with catalysis of Zinc chloride supported by anion- exchange resin. [89] Synthesis of Pseudo-Ionone catalyzed by macroporus anion exchangers. [90] Synthesis of Methyl-

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Ionone with macroreticular resins as catalyst [91] has been studied in the process of ion exchange.

In the study on catalytic shape-selective isomerization[92] molecular sieve were modified by chem., vapour deposition method to preparation shape-selective catalysts disproportion method –it was inferred from the results of alpha pinene isomerization catalyzed by these shape-selective catalyst, the kinetic diams of alpha pinene,terpinoline and limonene are approx > 0.68 nm ,0.68 nm and 0.58 nm respectively.

Production of isolongifoline from longifoline and its apparatus are disclosed. It is carried out by using macroporous strong acid type cationic exchange resin as catalyst, adding longifoline into macroporous strong acid type cationic exchange resin by mass ratio of longifoline and macroporous strong type cationic resin, reacting, filtering, removing macroporous strong acid type resin as catalyst and obtaining the isolongifoline. The apparatus consist of reactor and heating sleeve, the reactor is sleeved on the heating sleeve consist of sleeve and coil type heating element, the coil-type heating element is arranged on the sleeve. [93]

Conclusion

Using clays, hetropoly acids, and zeolite and Ion exchange resins catalyzed transformations of terpenoids proved a fruitful approach. The advantage of heterogeneous acid catalysts such as no acid wastes, facile treatment of the reaction mixture, catalyst regeneration and recycling etc.Catalyst reuse increases the overall productivity and cost effectiveness of chemical transformations while minimizing their environmental impact and fits most "principles of green chemistry. In acid media, terpenoids generally undergoes various transformations. The acid catalysts of the terpenoid transformations include various liquid Bronsted and Lewis Acids, Acid clays, Hetropoly acids, Zeolites,Ion- exchange resins etc. Montmorillonite clays were generally the most popular catalyst of pinenes isomerisation & transformations of pinenes in to camphene occurred predominantly on the Bronsted acid centers.   The isomerization of longifolene using montmorillonite clay K10 as catalyst at 120° C. Hetropoly acids (HPAs) have attracted interest as catalyst for clean synthesis of fine and specially chemicals. HPAs exhibit higher catalytic activity in various reactions of terpenoids such as hydration, acetoxylation, and isomerisation in heterogeneous catalysis by $H_3PW_{12}O_{40}$ (PW). - terpineol, in to more valuable isomers, - pinene

and longifoline can be converted in to camphene and isolongifoline, respectively. Metalloporphyrins, with structure based on the well known meso-tetraphenylporphyrin (TPPPH$_2$), are amongst the catalyst commonly studied. The porphyrin complexes (Metalloporphyrins) have been used in oxygenation of terpenes; these transformations have been studied in the presence of different oxygen atoms donor's oxidations under heterogeneous conditions. The magnesium (III) porphyrins have been used in the oxidation of   - pinene and   –terpinene. Zeolite has been playing a role in heterogeneous catalysis. Cobalt containing MCM-41 Zeolite Catalyst was used as a heterogeneous catalyst for the liquid-phase aerobic oxidation of isolongifoline, one of the most available sesquiterpenes. The hydration of turpentine was carried out, using macropore and strong acidic cation exchange resin Amberlyst 15 wet as catalyst. The Synthesis of nopyl with catalysis of Zinc chloride supported by anion- exchange resin. The Synthesis of Pseudo-Ionone is catalyzed by macroporus anion exchangers. The production of isolongifoline from longifoline is carried out by using macroporous strong acid type cationic exchange resin as catalyst.

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