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Synthesis of Isopulegol Through Cyclisation of Citronellal Using Solid Acid Catalysts: Catalytic Reaction Performance Evaluation and Process Parameters Optimization

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Abstract

The cyclisation of citronellal to isopulegol is a significant intermediate stage in the production of menthols. In this research work, the effects of acid treatment on montmorillonite clay have been investigated and used in citronellal cyclisation reactions. Furthermore, the effects of acid treatment and hetero-poly acid impregnation have been determined on the textural and catalytic properties of montmorillonite clay. The designed catalysts were characterized by XRD, N_2 sorption, and NH_3-TPD techniques. Acid treatment of montmorillonite resulted in the enhancement of surface area and pore volume. The catalytic activity and selectivity parameters were lessened due to the severe leaching of Al ions from tetrahedral crystalline structures (e.g., weakened structure and loss of acidity). Among all prepared materials, the heteropoly acid supported HCl treated montmorillonite catalyst was observed as a more active, stable, and selective catalyst that showed the highest catalytic performance in citronellal cyclisation under optimized process parameters. The catalytic activity and selectivity were enhanced with rising mesoporosity and acidity parameters due to HCl acid treatment and HPA impregnation.

***Keywords*:** Acid treatment, Catalytic activity, Citronellal cyclisation, Montmorillonite, Process Parameters.

Introduction

Citronellal (3, 7-dimethyl-6-octen-1-al) reactant is widely utilized for the production of fine chemicals. The citronellal reactant is transformed into isopulegol and menthol products through cyclisation and hydrogenation steps, respectively [1]. The menthol product has wide industrial applications in fragrances, pharmaceuticals, cosmetics, and tobacco preparation [2]. The annual menthol consumption is between 30 and 32000 metric tons, which is more than the overall manufacturing of menthol [3]. Numbers of complex hydrogenation reactions are available for menthol synthesis, but the main issues are less selectivity, reaction control, and reactants availability parameters.

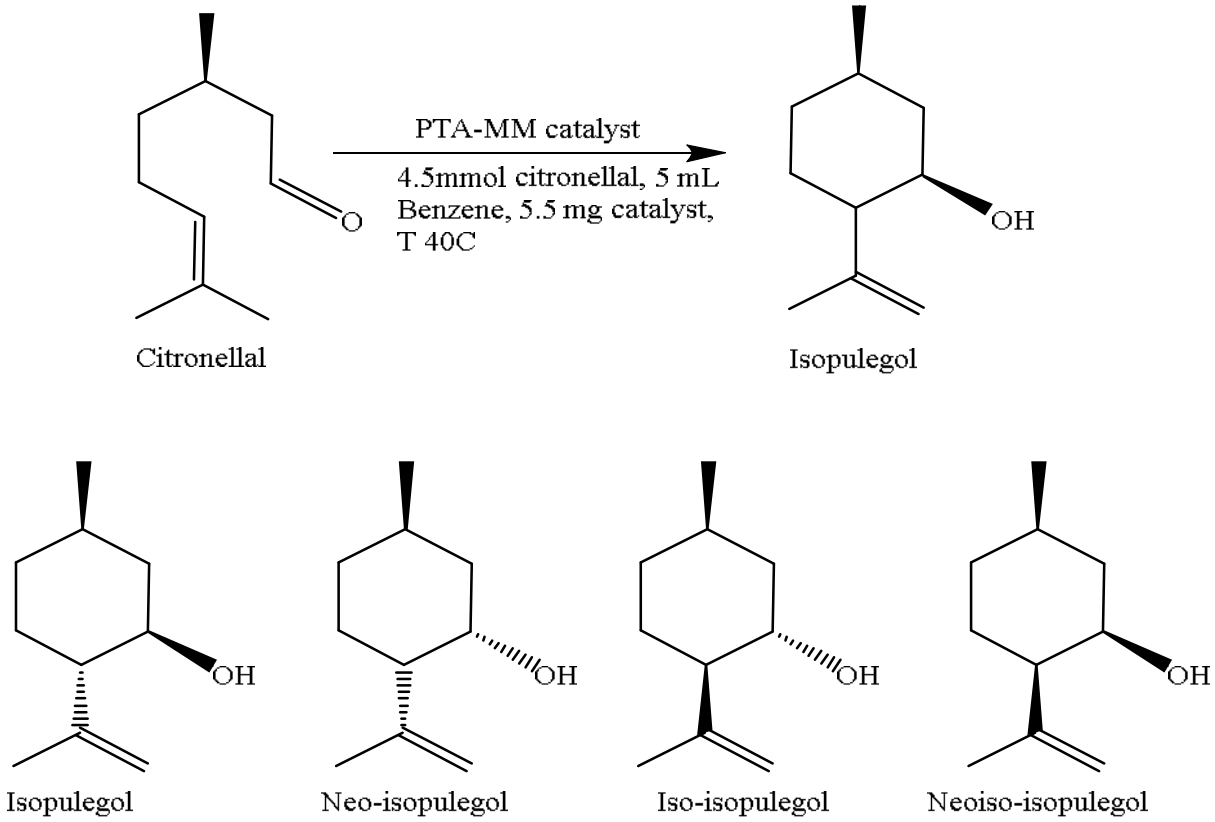
Menthol synthesis is two steps reaction: 1) cyclisation of citronellal to isopulegols, 2) then hydrogenation of isopulegol to menthols. Compared to other complex reactions, citronellal cyclisation is considered the simple and easy controllable reaction, which can produce a high yield of isopulegol and menthol at a low cost.

Many research workers have worked on various acidic nature catalysts, but their activity for cyclisation reactions was not found good as compared to desired. However, in other cases, the catalyst's lower stability and selectivity parameters are found as major issues in the proper designing of commercial catalysts [4]. In designing solid acid catalysts, numbers of acid sites (Lewis or Bronsted) are required as per the nature of chemical reactions. For the production of isopulegol, strong Lewis acid sites and weaker Bronsted acid sites creation on catalyst surface is required to give a high yield of isopulgol (cyclic product). Unbalanced acid sites may cause dehydration or deprotonation side reactions that result in a decrease in isopulegol yield. For citronellal cyclisation, a number of solid acid catalysts such as zeolites, mesoporous materials [5], solid Lewis acids [6], carbon molecular sieve [7], hydrous zirconia [2], heteropoly acid supported silica [8], inorganic fluorides [9], and heteropoly acid supported MCM-41[10] have been prepared and tested in citronellal cyclisation for a getting high yield/selectivity of isopulegol [9, 11]. According to the previous work, some acid catalysts were found inactive, less selective, and unstable in nature when these acid catalysts were doped with metals for the production of menthol [12-19]. Chuah *et al.* prepared solid acid catalysts that catalyzed side reactions such as dehydration, cracking, and etherification of isopulegol. They suggested that the presence of both Bronsted and Lewis acid sites is important for this selective reaction [20]. Yongzhong *et al.* designed "zirconium supported beta zeolite" catalysts and their modified versions. They studied the effects of solvent polarity on catalytic activity and selectivity. The reaction rate and selectivity parameters were found most dependent on Lewis and Bronsted acid sites of catalyst [21]. In addition, menthol production from citral or citronellal is a very complex job. This is a multistage reaction that contains multistage hydrogenation and cyclisation/isomerization reactions. The catalyst design as per chemical kinetics nature is a very difficult assignment. The first stage is to develop a highly active and more selective catalyst, and then 2^{nd} stage focuses on the stability and recyclability of the catalyst. There are many parameters such as narrow pore structure, unbalanced acid sites, and limited mass transfer/diffusion issues that affect the catalyst's performance and design. Due to the narrow pore structure of the catalyst, the mass transfer/diffusion rate becomes lower or negligible. The various treatment techniques such as desilication, dealumination, or leaching have been used to re-design internal morphology or pore structure. This research also focused on pore structure modification of narrow structure montmorillonite/clay using acid treatment. Further balanced acid sites (L/B) over the montmorillonite surface have been adjusted by a dope of heteropoly acid (HPA).

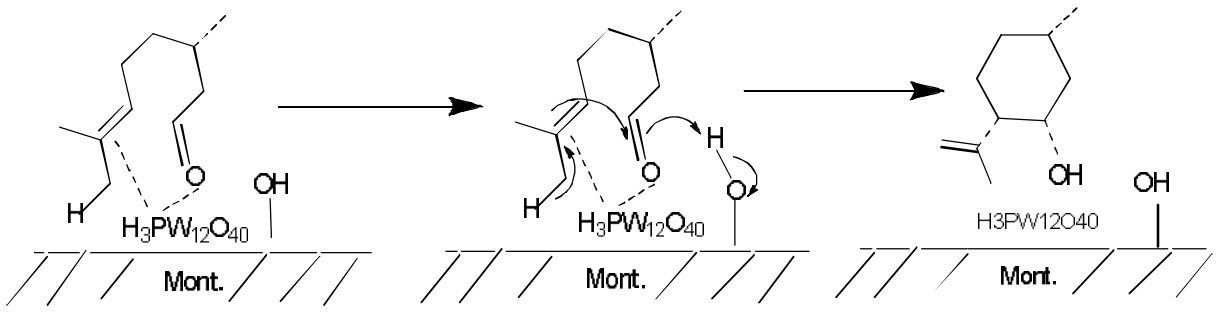
Further effects of process parameters have been analyzed on catalytic activity and selectivity of prepared novel catalysts. Further properly designed solid acid catalysts may help in menthol production with high selectivity. Furthermore, this research study focused on finding a correlation of catalytic properties with textural properties of the support. Further process parameters such as reaction temperature, catalyst amount, and substrate: solvent ratio were studied and

optimized for higher catalytic activity and isopulegol selectivity.

The objective of this research work was to evaluate catalyst preparation, reaction performance, and correlation with catalyst's textural properties and catalytic activity. Further, the effects of acid treatment of montmorillonite on catalysts' properties and activity have been studied in detail. In addition, the effects of process parameters optimization and characterization have been found out and correlated with isopulegol selectivity and activity.



Scheme 1. **Cyclisation of citronellal to isopulegol over solid acid catalysts**



Scheme 2. **Proposed reaction mechanism of citronellal cyclisation to isopulgol over heteropoly acid supported montmorillonite catalyst [4].**

Materials and Methods

Heteropoly acid (PTA, $H_3PW_{12}O_{40}.n\ H_2O$), montmorillonite (K10), (±) citronellal (≥95%, rest 5% contains isopulegol and 3, 7-dimethyl-1-octanol) were purchased from Merck (Darmstadt, Germany). Other chemicals such as nitrobenzene (99.5%), benzene, methanol (99.8%), HCl (70%), H_2SO_4 (95-97%), and HNO_3 (69%) were bought from Dae-Jung Chemicals (Gyeonggi-do, South Korea).

Catalyst Preparation

The commercial montmorillonite clay support (MMT) was purchased and modified with inorganic acids. The 10 g of montmorillonite was poured into each round bottom flask and 100 mL (4 M) of each HCl, H_2SO_4, and HNO_3 were added to each flask with a magnet bar. These flasks were fixed with a condenser for maintaining reflux. The flask reactors were heated at 80ºC for 4 h under water reflux conditions. After acid treatment, the slurries were washed with distilled water until they were neutral (pH=7.0). The samples were dried at 110 ºC in the oven for 24 h and calcined at 200 ºC for 2 h. After calcination, the calcined samples were labeled as HCl-MMT, H_2SO_4-MMT, and HNO_3-MMT. Further acid-treated montmorillonite sample was modified with impregnation of heteropoly acid. Various ratios of heteropoly acids have been doped over the surface of acid-treated montmorillonite samples using ethyl alcohol solvent at room temperature using wetness impregnation techniques. The doped heteropoly acid supported montmroillonite samples were evaporated and dried at 80 ºC for 5 h using a vacuum rotary evaporator [22].

Catalyst's Characterization Study

The catalysts were prepared and characterized by using XRD, N_2 sorption, and NH_3-TPD techniques. X-ray Diffraction characterization of some specific catalysts samples was done using Powdered X-ray diffraction (D/ Max 2200 Rigaku) using Cu Kα radiation at a fixed accelerating voltage (40 kV) and current (100 mA) within the 2θ range of 5°–60°. The pore structure characterization such as surface area, pore volume, and pore size distribution, was measured by nitrogen adsorption using a Micrometrics Tri-Star 3020. Before the characterization, all prepared samples were degassed at 200 °C for 3 h under vacuum conditions. The acidity of prepared catalyst samples was measured by NH_3-Temperature-Programmed Desorption (TPD) using an Auto-Chem 2920, Micrometrics, USA. Adsorption of NH_3 was performed at 50 °C temperature with a flow rate of 20 $cm^3\ min^{-1}$ for 45 min, followed by helium purging for 1.5 hours at room temperature to remove the physisorbed NH_3. The desorption process was recorded in the temperature range of 50–900 °C at a heating rate of 10 °C min^{-1} under a helium flow (20 $cm^3\ min^{-1}$), and the evolved NH_3 was monitored by TCD. In comparison with NH^3-TPD data, the acidity amount of samples was determined through the amine titration technique, as mentioned in our published work [22].

Citronellal Cyclisation

The catalytic citronellal cyclisation reaction was performed using a 10 mL glass reactor. Chemicals such as 4.5 mmol of (±) citronellal (≥95%), 0.2 mL nitrobenzene (standard reagent), 5 mL benzene solvent, and 50 mg catalyst were added into the reactor. Further details are described in our published work [22].

Results and Discussion

Catalysts Characterization

The XRD patterns in a wide-angle range of original montmorillonite, as well as acid-treated montmorillonite samples, are shown in Fig. 1. XRD spectroscopy of

montmorillonite (MMT) was similar to JCPDS, whereas, powder diffraction standard shows 2-theta angles of 5.8, 17.7, 19.8, 35.1, and 60. The montmorillonite (MMT) peaks intensity was reduced after each acid treatment. These values intensity reduction was majorly measured in hydrochloric acid and sulfuric acid treatments (Fig. 1). The acid treatment of montmorillonite with nitric and sulfuric acid weakened the crystal structure of montmorillonite. After acid treatment of original montmorillonite, some internal structural changes were observed from the XRD analysis of samples, and there might be changes in the cation exchange capacity values of montmorillonite. These changes in the XRD structure may suggest more removal of Al ions from the montmorillonite framework. The XRD structure of montmorillonite was maintained with HCl treatment as compared to other acid treatments. Fig. 1 shows changes in the XRD pattern afterward immobilization of HPA on hydrochloric acid-treated montmorillonite support. These XRD pattern changes imply that all HPA are successfully deposited on acid-treated montmorillonite and improved a little crystallinity of the supported catalyst. The intensity of the heteropoly acid peaks was very low, which may show its complete dispersion in the pores of support or small particle size of HPA, which could not be detected apparently (Fig. 1).

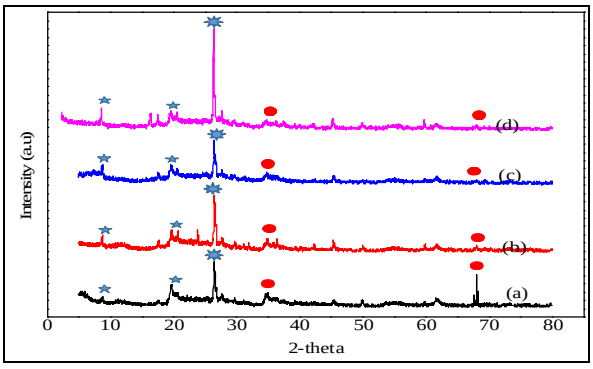


Figure 1. **XRD patterns of (a) Montmorillonite (MMT), (b) HCl-MMT (c) H_2SO_4-MMT (d) Pd supported PTA-HCl-MMT. Symbols show Si, ✹ and ● Al elements**

FTIR analysis shows the structures of original and acid-treated montmorillonite, as well as HPA, supported montmorillonite samples. The FTIR broad peak of montmorillonite was appeared to range between 960-1080 cm^{-1}. The infrared band of original montmorillonite at 3637 cm^{-1} displays the occurrence of stretched hydroxyl groups and cations from the corresponding octahedral sheet. The weak band at 3420-3429 cm^{-1} is indicative of water adsorbed on the MMT surface, and its existence was definite by the deformation band at 1637-1642 cm^{-1}.

Similar observations were recorded in all acid-treated samples. The hydroxyl groups intensity was reduced after each acid treatment. The band at 803 cm^{-1} intensity of MMT increased after each acid treatment, especially in HCl treatment (Fig. 2). The FTIR characterization of HPA supported montmorillonite is described in our recently published paper [22].

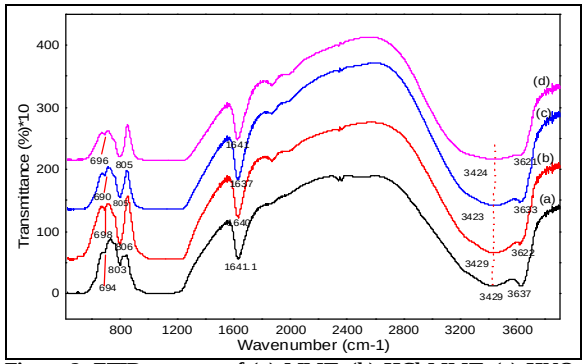


Figure 2. **FTIR spectra of (a) MMT, (b) HCl-MMT, (c) HNO_3-MMT and (d) H_2SO_4-MMT**

The N_2 sorption study also confirms the changes in surface area, pore volume, and pore size after acid treatment of montmorillonite. BET analysis shows improvement in pore volume and surface area of montmorillonite after acid treatment (Table 1). The BET surface area (207.65 cm^2/g) and pore volume (0.2416 cm^3/g) of original montmorillonite (MMT) increased to 231.73-242.41 m^2/g and 0.318-0.435 cm^3/g

respectively. In comparison to acid treatment results with XRD, HCl-treated MMT has maintained crystal structure with improved textural properties. With impregnation of (20 wt.%) heteropoly acid on hydrochloric acid-treated montmorillonite, the BET surface area and pore volume were reduced to 109.18 m^2/g and 0.231 cm^3/g, respectively, it may occur due to dispersion of HPA in the pores of montmorillonite and blocks the pores of the support. Furthermore, BET surface area and pore volume reduction take place with impregnation of more concentration (above than 20 wt. %) of HPA. According to the BJH plot, the pore size of original montmorillonite gradually increased with acids treatment, but HCl treatment increased pore size from 5.2 (52.1 Aº) was increased to 9.4 nm (94 Aº), but increased pore size was further reduced to 5.5 nm (55 Aº) with HPA loading (10 wt.%). Pore size was reduced due to the accumulation of HPA in the montmorillonite support and blocks their pore volume and surface area. The observed pore size range of the catalyst (5.2-9.4 nm) shows that the material is considered mesoporous. It lies in isotherm type IV that shows the mesoporous structure (Fig. 3).

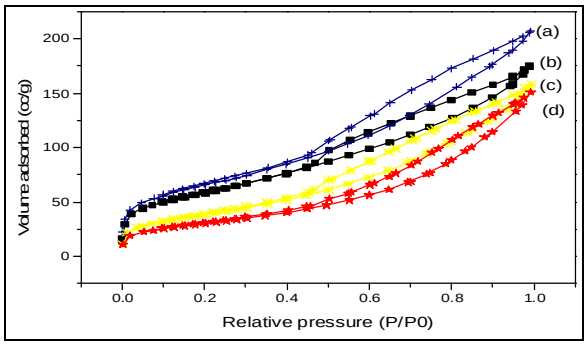


Figure 3. **N_2-adsorption-desorption isotherms of (a) HCl-MMT (b) HNO_3-MMT, (c) H_2SO_4-MMT, (d) HPA-HCl-MMT catalyst samples**

The precipitous rises of N_2 gas absorption were observed at P/P_0=0.4-0.5 of acid-treated montmorillonite and were endorsed to the occurrence of a uniform size of mesoporous.

The acidity strength of prepared samples was measured by the NH_3-TPD technique. The montmorillonite contains an acidity of about 0.31 mmol/g cat, which was further enhanced with acid treatments (0.44 mmol/g cat). It has been observed that nitric and sulfuric acid treatments could not enhance acidity efficiently because strong acids leached more Al ions from the montmorillonite framework and weakened crystal structure and acidity strength (6~16% decrease). Among acid treatments, hydrochloric acid treatment enhanced the acidity strength of montmorillonite because it might be due to less leaching of Al ions from the framework. Further acidity strength of HCl-MMT increased (0.44 to 1.02 mmol/g cat) with impregnation of HPA (Table 1).

Table 1. **Textural and acidic properties of prepared samples.**

Catalyst	BET surface area (m^2/g)[a]	Total pore volume (cc/g)[a]	dp nm	Acidity[b]
MMT	207.65	0.2702	5.2	0.31
HCl-MMT	231.73	0.318	9.4	0.44
H_2SO_4-MMT	204.16	0.435	8.53	0.26
HNO_3-MMT	242.41	0.369	6.08	0.29
HPA-HCl-MMT	109.18	0.231	5.5	1.02

[a]determined by BJH method
[b]determined by NH_3-TPD method. N_2 adsorption-desorption isotherms of prepared samples show the shape of hysteresis loops around from 0.47 to 0.98 of relative pressures.

Catalytic Performance Evaluation

In the initial stage, citronellal cyclization to isopulegol reaction was performed over different zeolites based catalysts such as zeolite X, zeolite Y, zeolite X-Y, ZSM-5, K-10, silica, alumina, and MCM-41. Similar process conditions were applied for all samples and the reaction was preceded for 3 h. The conversion of citronellal over zeolite X and Y was about 5 and 30%,

whereas, isopulegol yield was 7% and 15%, respectively, whereas; X-Y zeolite did not display any catalytic conversion of citronellal. In comparison with zeolites, ZSM-5 catalyst was tested, which gave approximately 21% isopulegol yield with 45% conversion. The catalytic activity of mesoporous materials such as MCM-41, SiO_2, and K10 montmorillonite was tested in citronellal cyclisation and compared with zeolites. MCM-41 is mesoporous and possesses some acidity, which helped in citronellal conversion and yielded about 40%. Similarly, the K10 montmorillonite catalyst gave 81% conversion and 51% selectivity (Fig. 4). However, catalytic conversion of citronellal over silica and alumina seemed almost negligible. The catalytic conversion and isopulegol yield have close interaction with materials properties. Interestingly, zeolites have good catalytic properties with a narrow pore structure, which limits mass transfer and diffusion rate. Due to this reason, the citronellal cannot diffuse inside pores of zeolites, so catalytic activity is negligible. In comparison with silica and alumina, they possess good textural properties but acidity strength is almost negligible. For citronellal cyclisation, the presence of acid sites over the surface of catalysts is important for getting cyclisation of citronellal.

Based on the requirements of citronellal cyclisation reaction, montmorillonite support was considered for a further research study, because it is cheap and available in abundant quantity, and possesses good catalytic properties. It is made of an aluminosilicate framework but it has some mass transfer limitations because of narrow pore structured properties, which can be resolved through post-treatment methods such as dealumination and desilication. This research focused on determining the effects of dealumination (acid-treatment) on pore structure, acidic and catalytic properties.

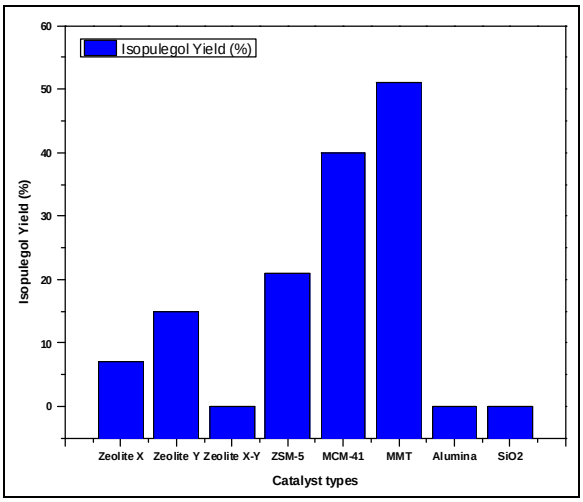


Figure 4. **Catalytic evaluation of different solid catalysts in citronellal cyclisation for the isopulego production (Reaction conditions: 4.5 mmol citronellal, 5ml solvent, 0.05 g catalyst, T 80 °C, time 3 h)**

Effects of acid treatments on montmorillonite

The catalytic activity and the selectivity of the support materials were investigated in cyclization of citronellal to isopulegols (Scheme-1). MMT shows good catalytic activity, whereas; isopulegol selectivity rate (51%) was lower than acid-treated montmorillonite samples (83-91%) at a conversion of 86-95% (Table 2). The weak catalytic performance of MMT is expected due to impurities, narrow pore structure, weak acidity with imbalanced acid sites ratio. Based on this limitation problem, montmorillonite was treated with different inorganic acids (HCl, HNO_3, and H_2SO_4) using similar conditions to develop more mesoporous material.

In basic reaction findings, citronellal cyclisation was carried out in the absence of solid acid catalyst. The reaction was preceded for a long time (3 h), but no more citronellal conversion was observed. This reaction test confirms that citronellal cyclisation is catalyzed reaction. The reaction was performed in a glass reactor without the use of solvent. The fixed amount of montmorillonite

catalyst was poured into the reaction mixture and the reaction was preceded for 3 h in the absence of solvent. The reaction sampling was done at some interval of time. The reaction data suggests that citronellal was catalyzed to isopulegol with the formation of side products. It gave 65% citronellal conversion and 38% isopulegol selectivity. The less formation of isopulegol might be due to mass transfer limitation (highly concentrated reactants). Further citronellal cyclisation was preceded in the presence of the catalyst and benzene solvent. The catalytic activity (conversion 81%) and isopulegol selectivity (51%) enhanced (reactant's concentration was diluted with solvent, which helped in fast mass diffusion). The reaction conditions were optimized. Further the effects of catalyst and solvent addition on catalytic activity and selectivity were inspected.

Table 2. **Performance of prepared catalysts in citronellal cyclisation.**

Samples	Solvent	Reaction time (h)	Conversion (%)[a]	Selectivity (%)
No Catalyst	Benzene	3.0	5	0
MMT	No solvent	1.0	65	38
HCl-MMT	No solvent	1.0	78	53
H_2SO_4-MMT	No solvent	1.0	69	41
HNO_3-MMT	No solvent	1.0	72	46
MMT	Benzene	1.0	81	51
HCl-MMT	Benzene	1.0	95	91
H_2SO_4-MMT	Benzene	1.0	86	83
HNO_3-MMT	Benzene	1.0	90	85
HPA-HCl-MMT	Benzene	0.5	100	97

[a]4.5 mmol citronellal, 5 g benzene, 0.2 mL nitrobenzene, 50 mg catalyst

In Table 3, the best results of various solid acid catalysts (previous work) have been shown. This showed that many catalysts were more active but less selective or vice versa. The worst catalytic performance might be connected with the desired number of active acid sites. In Table 3, various catalysts showed catalytic performance and isopulegol yield. Similarly, all samples' catalytic activity was evaluated in citronellal cyclization reaction at similar process conditions without the use of solvent. Without the use of solvent, molecule's movement, diffusion, as well as adsorption-desorption rates, became slow down and product cracking chances were increased and finally less than 50% isopulegol selectivity was recorded at full conversion (Fig. 5). It shows that solvent presence in a reaction is most important because it helps in boosting a molecule's movement, diffusion, and adsorption-desorption rate. The solvent can dissolve reactant molecules and promotes them with strong diffusivity and reactivity. Many side reaction products e.g. acetals of citronellal, isopulegol ethers, menthoglycol were determined by GC-MS during the reaction study.

Table 3. **Published data on citronellal cyclization reaction.**

Catalyst	Conversion (%)	Overall selectivity	Ref.
Al-MSU-50	27.8	87	Yougzhong [21]
Zr-beta-100	59.7	98	
ZrO_2-0-300	11	94	Chuah [20]
ZrO_2-4-500	0	85	
Montmorillonite	98	19	
MgF_2-40	24.3	75	Coman [12]
MgF_2-57	46.6	76.4	
MgF_2-87	5.7	16	
MgF_2-100	3	36.7	
S-ZrO_2[650]	95	35	Yadav [8]
S-ZrO_2[230-350]/Benzene/CMS	91	65	

The catalytic performance of MMT was not satisfactory; the reason for the lack of performance might be the narrow pore structure and weak acidity of montmorillonite. Literature review supports that citronellal cyclisation occurs over Lewis/Brønsted acid sites of catalyst [15-19].

In order to resolve the mass transfer limitation problem of MMT, our research focused on improving the pore structure and acidity of MMT with the use of inorganic acids. Therefore, montmorillonite was treated

with hydrochloric acid, nitric acid, and sulfuric acid. The catalytic activity and selectivity improved with enhancement in surface area and pore size [23-25]. This change may result in high molecules diffusion rate and high adsorption-desorption rate of reactants/products in catalyst support. It was seen as possible by major changes in montmorillonite internal structure and surface properties after acid treatment (Table 1).

This acid treatment of MMT helped in enhacement of mesoporosity and surface area (Table 1). Due to increased high surface area and wide pores, adsorption and desorption rates were improved which resulted in higher activity, reactivity, and selectivity [26-27].

Effects of HPA loading on mesoporous montmorillonite

The acid treatment technique shows positive changes in montmorillonite structure, surface, and acidic properties. HPA concentration was immobilized on the surface of montmorillonite to verify that active acid sites on the surface have a definite role and no resistance to mass transfer. On increasing HPA loading (e.g. more than 20%), the surface area and pore volume were reduced due to blockage of montmorillonite pores. With the impregnation of HPA, the acidity of support was enhanced. The catalytic activity and selectivity were enhanced with increased acidity, whereas reduction in surface area and pore size of montmorillonite has no effect. The catalyst selectivity and surface properties were changed with HPA loading.

Furthermore, catalytic and acidic properties of mesoporous montmorillonite were improved by deposition of phosphor-tungstic acid and showed improvement in isopulegol selectivity (97%) (Table 2), it is optimum selectivity by compared described herein [20-21, 28]. It was a novel point that HPAs were found best for the improvement in catalytic and acidic properties. In addition, investigations were carried out to determine the catalytic effects of lower HPA concentration loading on montmorillonite support. The isopulegol yield was decreased with an increase in HPA loading higher than 10 wt.%. Finally, 10% HPA supported mesoporous montmorillonite catalyst was further investigated. It is thought that HPA are deposited successfully on the surface of montmorillonite and bring overall changes into the surface, catalytic and acidic properties, and work as bifunctional active catalysts.

Effects of reaction period on catalytic citronellal cyclization

Prepared catalysts were analyzed in citronellal cyclisation with respect to time, as shown in Fig. 5. The catalytic conversion of citronellal increased w.r.t time, and all citronellal will be transformed to isopulegol. Acid treated and HPA supported samples showed good catalytic activity.

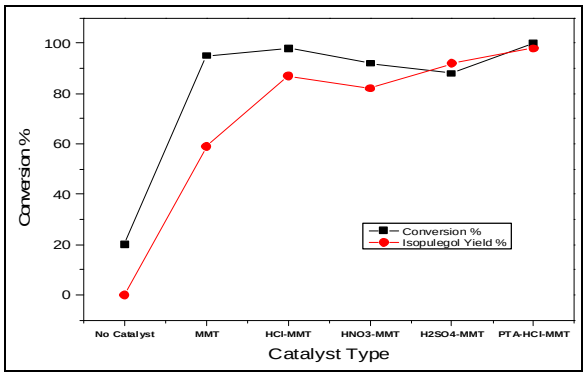


Figure 5. **Performance of different solid catalysts in citronellal cyclisation with respect to time**

Reaction mechanism over HPA supported montmorillonite

Heteropoly acids are well-built Bronsted acids and comprise different hydroxyl groups on their surface. The presence of strong Lewis acid sites and

medium Bronsted acid sites help in the protonation and deprotonation of citronellal and transform into isopulegol. Both acid sites play a vital role in citronellal cyclisation. Improper balance of both sites may cause side reactions formation. Experimental and literature review suggests that acidity strength boosts up reaction rate and desired acid sites (L/B) insist in product formation (selectivity). Cyclization of citronellal can be possible through carbonyl group protonation of citronellal, after that, intermolecular rearrangement is carried out to make stable deprotonation and carbocation to produce isopulegol [12]. As far as Scheme 2 is concerned, the citronellal coordinates through electron-rich double bond and aldehyde oxygen atom lying on heteropoly acid particles. This contact helped to form a ring through carbonyl-ene (C-C) reaction. As far as the transition state of reaction is concerned, oxygen atom protonation occurs through a neighboring Bronsted hydroxyl group from the heteropoly acid surface. After hydrogen atom elimination from the isopropyl group, the formation of the ring is closed to form isopulegol. After cyclization of citronellal, Lewis and Bronsted functional groups were recovered into the same position. Through bimolecular dehydration of isopulegols other side products are formed [25-30]. Maximum water formation through isopulegol dehydration causes to a generation of limited methyl glycol ether [13].

From overall results and discussion, it has been summarized that montmorillonite possesses a narrow pore structure and weak acid sites. Acidic treatments with various inorganic acids result in more increase in surface area, pore volume, and acidity. Sulfuric acid treatment of montmorillonite results in severe Si leaching and XRD structure collapse. Among acid treatments, HCl was found more suitable for maintaining structure and acid sites. Heteropoly acid doped HCl- treated montmorillonite has shown a good catalytic activity and selectivity as compared to other prepared catalysts.

Conclusion

In this research work, montmorillonite's textural and acidic properties were improved with an acid treatment and HPA impregnation. Acid treatment increased surface area and pore volume with the elimination of Al ions from the framework. Further acidity of support enhanced with HPA impregnation. The catalytic activity and isopulegol selectivity enhanced with a rise in surface area and acidity. The increase in acidity has a direct influence on isopulegol selectivity. The hydrochloric acid treatment produced mesoporous support and maintained structure, whereas acidity strength improved with HPA impregnation. HPA-HCl-MMT catalyst has shown a good catalytic activity (e.g., 100% citronellal conversion) and high isopulegol selectivity (97%) within a short reaction period (0.5 h). The prepared catalysts were found inactive and less selective in citronellal cyclisation without solvent. The catalytic activity and selectivity have improved with more surface area and Lewis acidity under a stable XRD structure.

Conflict of Interest

The authors declare that they have no conflict of interest.

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