

Heterogeneous Catalytic Conversion of Citronellal into Isopulegol and Menthol: Literature Review

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Abstract

The conversion of citronellal into isopulegol is a key route in the production of a number of important chemicals. In the perspective of green conversion, the use of a heterogeneous catalyst is superior due to its ease in separation and reusability, so it facilitates a highly economical conversion. In this review, we examine the use of some transition metals in cyclization reactions, which are suitable for citronellal conversion into isopulegol, and consider the potential progress in clay-based catalysts. The structure of clay which potentially provides the porosity by modification and supporting active metal is proposed to be the low-cost catalyst for the conversion. As other mechanism by porous materials-supported metal, the porosity of clay support contributes to conduct the surface adsorption mechanism and the Bronsted acid supply, meanwhile the metal acts as active site for cyclization, and in the one-pot conversion into menthol, as both cyclization and hydrogenation.

Keywords

Citronellal, Isopulegol, Menthol, Catalysis Process

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1. INTRODUCTION

Along with the increasing demand for valuable chemicals in drug, food, and therapeutics applications, new strategies are developing for exploring raw materials derived from natural products, including essential oil derivative products (Sharma et al., 2019). In the pharmaceutical industry, the search continues for new bioactive compounds derivatives from essential oil products. One of the secondary metabolites that plays a role is citronellal. Citronellal has the potential to be used as a raw material for natural medicine and anticancer drugs (de Sousa, 2015; Lenardão et al., 2007). Citronellal is known to be cheap, readily available, and a very versatile starting material for some organic syntheses, including the asymmetric synthesis of chiral compounds used for producing aroma products such as pheromones, perfumes, and essences (da Silva et al., 2004; Jung et al., 2012; Yadav and Lande, 2006). Some processes for citronellal conversion play important roles for such platforms, including the strategic steps of extraction, characterization, racemic separation, and catalytic conversion. In addition to its direct use in therapeutics, citronellal is used in conversion reactions to obtain its important derivatives (Jung et al., 2012).

The isomerization of citronellal into isopulegol, the reduction into citronellol, and the direct and indirect conversion into menthol are valuable reactions in industry. For example, con-

sidering the world's large consumption of menthol in flavors for food and scents for toiletries, it would seem that menthol will remain in high demand. In the perspective of sustainability and increasing process efficiency, the optimization of citronellal extraction and conversion, including catalytic conversion, with intensified procedures is considered a crucial point (Knirsch et al., 2010). This review discusses the facts about, potential developments in, and optimization of citronellal extraction and conversion. As the main route in menthol production, catalytic conversion of citronellal into isopulegol and menthol is highlighted. Numerous papers have reported using heterogeneous catalysts for the single conversion of citronellal to isopulegol and the one-pot conversion into menthol (Adilina et al., 2015). The combined transition metal and solid supports were functionalized within the conversion mechanism.

2. CITRONELLA OIL: SOURCE AND EXTRACTION METHOD

Citronellal is a tradename of 3,7-dimethyl-6-octenal (structure is presented in Figure 1). Citronellal is a monoterpene, predominantly formed by the secondary metabolism of plants, which is usually derived as an essential oil through distillation and extraction. Citronellal, along with other terpenes such as citral, geranial, linalool, and citronellol, is typically isolated from more than 30 plants that produce essential oils (Lenardão

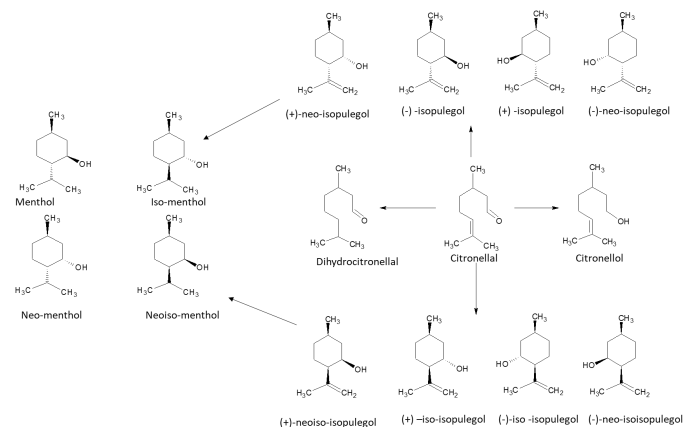


Figure 1. Conversion of Citronellal

et al., 2007). Table 1 presents some methods for citronella oil extraction.

The predicted annual production of citronella oil is around 2300 metric tons, and derived from many sources such as *Cymbopogon nardus*, *Cymbopogon citronella*, and *Cymbopogon winterianus* (Hamzah et al., 2013; Salea et al., 2018). These plants are easily cultivated with no specific requirements, increasing the ease with which citronella oil can be produced. Generally, the citronellal is present together with other components such as citral, neral, and terpenes. Two types of citronella oil are known commercially: Ceylon citronella oil, obtained from *Cymbopogon nardus* (inferior type), and Java type citronella oil obtained from *Cymbopogon winterianus* (superior type). The Ceylon chemotype consists of geraniol (18–20%), limonene (9–11%), methyl isoeugenol (7–11%), citronellol (6–8%), and citronellal (5–15%). The Java chemotype consists of citronellal (32–45%), geraniol (11–13%), geranyl acetate (3–8%), and limonene (1–4%) (Salea et al., 2018).

Different methods of distillation have been reported, such as extractive distillation, hydrodistillation (HD), steam distillation, and Soxhlet extraction, along with their process intensification strategies. Hydrodistillation, considered to be the most traditional method, has many intensification procedures, for example, ohmic-assisted hydrodistillation (OAHD), which is the combination of ohmic heating and hydrodistillation (Gavahian et al., 2018). OAHD has been reported as an effective method to enhance extraction performance by faster heating compared to other methods. Heat inside the materials is generated and the temperature is raised faster in OAHD than in conventional heating methods (Gavahian et al., 2018). This experiment reported by Gavahian et al., 2018 revealed an increase in yield of valuable compounds from *Cymbopogon* leaves, including a 3.6% higher yield of citronella oil compared to conventional distillation. Another similar enhancement of hydrodistillation is microwave-assisted hydrodistillation (MAHD). The effective molecular heating within the essential oil extraction by MAHD reduced the extraction time by 67% when compared to conventional distillation (Milone et al., 2000). The use of MAHD for

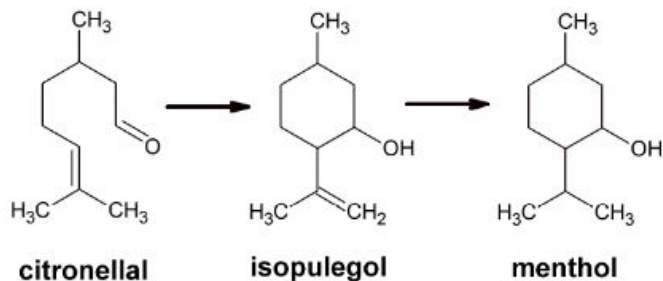


Figure 2. Synthesis of Menthol from Citronellal (Plöber et al., 2016)

citronellal extraction from *Cymbopogon citratus* produced higher yields and faster extraction times compared to conventional distillation: MAHD gave a yield of 0.35% v/w for a 90-minute extraction time, while conventional distillation gave a yield of 0.15% v/w for a 360-minute extraction time (Tran et al., 2019).

The intensification process of extraction can be performed with supercritical carbon dioxide, microwave irradiation, and sono-hydrodistillation (Hamzah et al., 2013; Solanki et al., 2018). Various optimum conditions involve parameters such as temperature, pressure and raw material loading. The significant increase in yield is due to the increase in density and solvency power, and it depends on operating parameters and the solvent. For example, the supercritical carbon dioxide extraction of citronella grass by compressed propane exhibited an increased kinetic constant and equilibrium yield (Guedes et al., 2018).

Compressed propane showed a higher equilibrium yield and kinetic constant than supercritical CO₂ under similar conditions (40°C and 6–9 MPa). However, supercritical CO₂ is a non-toxic and lipophilic alternative solvent with applicable critical temperature and pressure in industrial practice. The addition of ethanol to the solvents increased both equilibrium and kinetic properties even more, because the co-solvent interacts with the polar fraction, playing a complementary role along with the non-polar propane or CO₂. It is important to mention that the best results were obtained for the runs using a compressed propane solvent at 60°C and 2 MPa and supercritical CO₂ (solvent) with ethanol (co-solvent), with an ethanol-to-raw-material mass ratio of 1:1.

3. CITRONELLAL CONVERSION INTO ISOPULEGOL AND MENTHOL

As shown in Figure 2, citronellal can be converted into isopulegol, neoiso-isopulegol, citronellol, iso-isopulegol, neo-isopulegol, and menthol.

The conversion of citronellal into isopulegol is a pathway in the production of menthol, which is widely utilized in the pharmaceutical, soap, and toothpaste industries Raut and Karupayil (2014). Isopulegol has been reported as a good antioxidant and anti-inflammatory (Ramos et al., 2020), antihyperlipidemic (Kalaivani and Sankaranarayanan, 2019), analgesic (Kalaivani and Sankaranarayanan, 2019), and antitumor agent

Table 1. Some Methods for Citronella Oil Extraction

Source	Extraction method	Remark	Reference
<i>Cymbopogon nardus</i>	Ohmic-heated hydro-distillation, hydro-distillation, and steam distillation	The maximum amount of extracted oil yield by ohmic heated hydro-distillation was 7.64 mL/kWh, by hydro-distillation was 3.87 mL/kWh, and by steam distillation methods was 1.69 mL/kWh, respectively	(Hamzah et al., 2013)
<i>Cymbopogon citronella L</i>	Supercritical CO ₂ extraction (SFE)	The highest essential oil yield was predicted at extraction time 120 min, extraction pressure 25 MPa, extraction temperature 35°C, and CO ₂ flow 18 L/h for the SFE processing	(Wu et al., 2019)
<i>Cymbopogon winterianus Jowitt</i>	Manual extraction and hydro-distillation	Average percent yield in the manual extraction and hydro-distillation procedure was 0.8 and 1% respectively, which was better as compared to steam distilled oil (0.7%)	(Wany et al., 2013)
<i>Cymbopogon winterianus Jowitt</i>	Sono hydrodistillation	The optimum yield of oil was obtained as 4.118% (w/w) at 21 min extraction time, and 5 g solid loading	(Solanki et al., 2018)
<i>Taiwanese citronella grass</i>	Hydrodistillation (HD) and ohmic-assisted hydrodistillation (OAHD)	HD and OAHD gave similar yield, but OAHD saved 46% and 79% of the process time and energy, respectively.	(Gavahian et al., 2018)
<i>Cymbopogon citratus</i>	Microwave-assisted hydrodistillation (MAHD)	MAHD produced higher yield and faster time (0.35% v/w, 90 min) compared to conventional distillation (0.15% v/w, 360 min)	(Moradi et al., 2018)
<i>Citronella grass</i>	Supercritical CO ₂ extraction	The supercritical carbon dioxide extraction of citronella grass by compressed propane exhibited the increased kinetic constant and equilibrium yield	(Guedes et al., 2018)
<i>Cymbopogon nardus</i>	Supercritical CO ₂ extraction	High selectivity was obtained at 353.15 K and 18.0 MPa, with a more pure essential oil	(Silva et al., 2011)
<i>Cymbopogon winterianus</i>	Supercritical CO ₂ extraction	The highest citronella oil yield (3.206%) was achieved at a factor combination of 15 MPa, 50 °C and 180 min	(Salea et al., 2018)

Table 2. Mechanism of Intramolecular Cyclization Reactions in Various Catalysts

Catalyst	Compound	Mechanism	Target Compound	Conversion (%)	Reference
PBu ₃	N-allylic	Intramolecular Cyclization	α -amino nitril	-	(Zheng et al., 2016)
Cu(II)	(1,4 phenylene)-bisguanidines	Intramolecular Cyclization	benzodiiimidazole-diylidenes	99	(Mesias-Salazar et al., 2020)
Cu(I)	(1,4 phenylene)-bisguanidines	Intramolecular Cyclization	1-Aryl-1H-benzotriazole	97	(Liu et al., 2010)
Au(III)	α -Pyrroles	Intramolecular Cyclization	Pyrrolopyridinones and Pyrroloazepinones	68	(Li and Lin, 2015)
Fe(II)	Alkynes and Thiosalicylic Acid	Intramolecular Cyclization	1,3-oxathiane derivative	98	(Sonehara et al., 2017)
Rh(III)	Isoquinolone	Intramolecular Anulation	Indolizidine	65-77	(Xu et al., 2012)
Pt(II)	o-Isopropyl-substituted Aryl Alkynes	Intramolecular Cyclization	Indenes	-	(Wang et al., 2014)
Cs(III)	2-Bromoindoles	Intramolecular Cyclization	2-(gem-bromovinyl)-N-methylsulfonyl-anilines	-	(Li et al., 2013)
Rh(III)	Arylnitrones	Intramolecular Cyclization	Indolines	-	(Liu et al., 2016)
Ti(IV)	Isatins and 5-methoxy oxazole	Cyclization	spiro[3,3'-oxindoleoxazoline]	>99	(Badillo et al., 2011)
Zr(II)	Citronellal	Intramolecular Cyclization	Isopulegol	-	(Tobisch, 2006)
Zn(II)	Citronellal	Intramolecular Cyclization	Isopulegol	94	(Imachi et al., 2007)
Ru(III)	Citronellal	Cyclization and Hydrogenation	Menthol	80	(Azkaar et al., 2019)
Pt(II)	Citronellal	Cyclization and Hydrogenation	Menthol	85	(Azkaar et al., 2019)
NiS	Citronellal	Cyclization and Hydrogenation	Menthol	100	(Cortés et al., 2011)

(Jaafari et al., 2012). Isopulegol is also the intermediate for the synthesis of the anti-influenza compound octahydro-2H-chromenes Ilyina et al., 2021 and bioactive 2H-chromene alcohols as an antiviral agent (Laluc et al., 2020). Exclusively, isopulegol, especially (-)-isopulegol, is the starting compound in the production of menthol, which is a compound in high demand throughout the world (Coman et al., 2009; Plöber et al., 2014). Menthol is of prime importance in flavoring and pharmaceutical applications, as it elicits cooling and “fresh” sensations. Menthol is a chiral compound that can occur as eight possible stereoisomers: (\pm)-menthol, (\pm)-neomenthol, (\pm)-isomenthol and (\pm)-neoisomenthol. Of these, (-)-menthol is the product of interest.

At the industrial level, menthol production is performed by the Takasago process, which involves citronellal isomerization on an aqueous ZnBr₂ catalyst (Brunner, 2020; Nicolaou et al., 2000). The conversion of citronellal into isopulegol consists of acid-catalyzed cyclization, and the conversion of isopulegol into menthol includes hydrogenation (Figure 2).

Instead of enzymatic conversion (Bastian et al., 2017), isomerization by a chemical catalyzed process, which takes on the role of acid catalysis, is chosen due to the effectiveness of

the isomerization mechanism (Shah et al., 2018). In terms of energy efficiency, selectivity, and repeatability in the industrial scale, these conversions require effective catalytic processes and catalysts. In previous research and industry alike, citronellal isomerization and cyclization took place with a variety of homogeneous catalysts, but the catalysts often created disposal problems and were difficult to separate and recover (Guidotti et al., 2000; Vetere et al., 2002). Using the green chemistry perspective, the replacement of homogeneous catalysts with heterogeneous catalysts, in which the phase of the catalyst and reactants differ in form, is a viable alternative.

The mechanism of heterogeneous catalysis consists of the surface reaction, which reduces the activation energy of the reaction, as schematically represented in Figure 3.

The capability of heterogeneous catalysis to conduct adsorption of the reactants is the main point for the mechanism, and as it happens, the surface interaction among the adsorbed reactants is the crucial step for finally producing and releasing the products. The transition metals and their combination with solid supports are widely used, adapted with the characteristics of the reaction. As the citronellal conversion into isopulegol involves the acid catalysis mechanism, the transition metals such

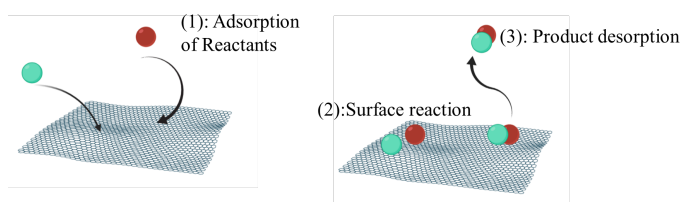


Figure 3. General Mechanism of Surface Reaction in Heterogeneous Catalysis

as ruthenium (Ru), Pt, Zr, and Ir were reported to be effective due to the availability of the Lewis acid sites. The availability of the d-orbital of the transition metal acts as a Lewis acid, which is capable of forming a bond with a π -electron of the double bonds of the reactant (citronellal). In separating this way, the conversion of isopulegol into menthol is through a hydrogenation mechanism, which in particular involves the capability of the catalyst to adsorb hydrogen (H_2). Some metals such as Ni, Pt and Au were reported to have excellent activity for this mechanism (Azkaar et al., 2019; Plöber et al., 2014). The combination of Lewis acidity from transition metals and the solid support consisting of Brønsted acidity and a high surface area gave an excellent improvement in yield and effectivity of the reaction. The solid supports provide not only stability in sites for reactant adsorption, but also, especially for the porous materials, an advantage in the catalyst stability and reusability. In addition, heterogeneous catalysts allow for regeneration and reusability, and some specific heterogeneous catalysts can provide direction for increasing the selectivity of the structure of certain products and the properties of the catalyst (Coman et al., 2009). To our knowledge, the review on heterogeneous catalytic conversion of citronellal into isopulegol and menthol is not yet presented. Considering the importance of isopulegol as intermediate for many compounds, and menthol in various applications, the aim of this review is to discuss potential heterogeneous catalysts in green conversion of citronellal to isopulegol and menthol.

4. CITRONELLAL CONVERSION INTO ISOPULEGOL

Citronellal conversion into isopulegol possesses a strategic pathway, one route of which leads to the production of menthol, consisting of two processes: citronellal cyclization and hydrogenation. In addition to preventing unwanted hydrogenation of citronellal, dimerization and defunctionalization (forming p-menthenes and p-menthanes), the challenge of using heterogeneous catalysts lies in the formation of diastereoisomers, namely isopulegol, iso-isopulegol, neo-isopulegol, and neoiso-isopulegol, as shown in Figure 4 (Plöber et al., 2016).

Although in industrial applications the mechanism of the citronellal cyclization reaction is still under debate, one proposed mechanism of the cyclization reaction occurs through protonation of the citronellal carbonyl group, which takes place after a stable carbocation is formed by intramolecular rear-

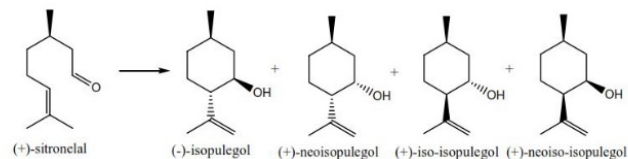


Figure 4. Citronellal Cyclization Gives Four Diastereoisomers (Vandichel et al., 2013)

angement, and ends with the deprotonation that produces isopulegol (Makiarvela, 2004).

The Takasago process, in which (-)-menthol is produced by the hydrogenation of (-)-isopulegol obtained from (+)-citronellal through acid catalyzed cyclization, is an important reaction in pharmaceutical industries (Cortés et al., 2011). The mechanism includes the ene-cyclization of (+)-citronellal to (-)-isopulegol over aqueous $ZnBr_2$ as a homogeneous catalyst, which causes a large amount of waste due to its non-regenerability. In order to make the process commercially attractive, synthesis of isopulegol with high stereoselectivity for the isomer (-)-isopulegol is important. Many studies highlighted that the selectivity is closely related to Lewis acidity (Shah et al., 2018; Milone et al., 2000; Shieh et al., 2003). With this background, most methods of the synthesis of heterogeneous catalysts were focused on activity, selectivity and stability, mainly by anchoring or immobilizing acid sites on stable inorganic materials. Such porous media as silica-alumina and silica-based materials were reported to be good supports (Shieh et al., 2003).

Combined experimental and theoretical studies reveal that the catalytic mechanisms and characteristics play a role in evaluating the catalyst performance and the selectivity of Lewis acids toward the desired stereoisomers (Sekerová et al., 2019). Some of the Lewis acid catalysts used are Zn, Zr, Ti and a Ni-based catalyst in supported form (Chuah et al., 2001; Fatimah et al., 2008; Guidotti et al., 2000; Jimeno et al., 2013). The result is that a Lewis acid catalyst becomes the main factor that contributes to the selectivity and catalytic activity of the cyclization reaction (Vandichel et al., 2013). A Lewis acid can act as an electron pair acceptor, as $ZnBr_2$, $ZnCl_2$, and ZnI_2 can act as catalysts for citronellal cyclization (Nisyak et al., 2017). The mechanism of citronellal cyclization is shown in Figure 4.

One type of Lewis acid catalyst is the zirconium-based catalyst. The results of research by Chuah et al., 2001 showed that zirconium hydroxide and zirconium phosphate catalysts also have activity and selectivity in the cyclization reaction of citronellal to isopulegol. The presence of Lewis and Brønsted acid catalyst sites is very important in the citronellal cyclization reaction, as depicted in the reaction mechanism proposed in Figure 5 (Álvarez-Rodríguez et al., 2012; Fatimah et al., 2014; Ravasio et al., 2000; Sudiarmanto et al., 2017).

The mechanism begins with the formation of a citronellal coordination bond to a Lewis acid through free electrons of carbonyl O atoms and π electrons of citronellal alkenes to Zr

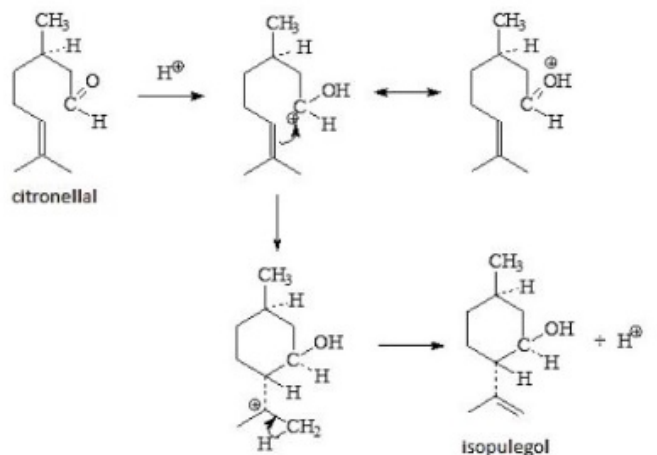
Fig. 2. Mechanism of citronellal cyclization⁷

Figure 5. Mechanism of Citronellal Cyclization (Tursiloadi et al., 2015)

atoms, followed by protonation of the Bronsted acid ($-Zr-OH$) sites against citronellal carbonyl O atoms (Chuah et al., 2001).

In line with the previous results, the conversion of citronellal to isopulegol was successfully conducted through a cyclization mechanism with a $ZnBr_2/\beta$ -Zeolite catalyst (Balu et al., 2010). The result is that the $ZnBr_2/\beta$ -Zeolite catalyst provides better activity than the β -Zeolite catalyst alone, where for $ZnBr_2/\beta$ -Zeolite the conversion value of citronellal to isopulegol is 100%, with a selectivity to isopulegol compounds of 75.28% at 120°C and a reaction time of 60 minutes. By a similar mechanism, $ZnBr_2/SiO_2$ catalyzed citronellal oil conversion gave a selectivity to isopulegol of 94.35%, and a conversion of 96.44% (Nuryanti et al., 2019). The mechanism of the cyclization reaction involves the formation of a ring compound from the chain by the formation of new bonds. The cyclization reaction is an intramolecular reaction where the reaction occurs in the molecule itself. The factors that influence the relationship between structure and reactivity intramolecularly include: induction, resonance, steric effects and hydrogen bonding. The intramolecular cyclization mechanisms in various metal catalysts are presented in Table 2. It is seen that the presented reaction conversions are quite high (68–100%), which further confirms that the conversion is related to the effective interaction between the metal catalyst and the π -bonds of the organic molecule (Li and Lin, 2015).

Based on the study of density functional theory (DFT), the transition state is coming from the linking between the active sites of the metal catalyst and the π -bonds. The bonding results in the potential energy surface near the stationary point and involves the activation of C=C bonds (double or triple bonds). The possible charge distribution among the resonance structures of molecules will lead to electron-rich properties of the internal alkyne carbon, which is thus more nucleophilic than the carbonyl carbon. The increasing energy facilitates the

1,2-migration of the internal alkyne carbon from the pyrrole's α - to β -carbon. The shifting energy also accelerates the interaction with hydrogen in the subsequent hydrogenation step (Li and Lin, 2015).

Table 2 shows some transition metals in the cyclization mechanism, especially in the regioselective organic synthesis. The presence of the active site provides transformation and indicates a highly convergent route to a wide variety of carbocyclic and heterocyclic structures. The PB_u_3 catalyst acts as a Lewis base to strengthen the nucleophilicity of the active reaction site (Zheng et al., 2016).

In addition, the cyclization reaction can be carried out with Lewis and Bronsted acid catalysts. Lewis acidity plays a role in providing coordination bonds for unsaturated metal ions, whereas Bronsted acidity plays an important role not only as an activating agent, but also in controlling the diastereoselectivity of reactions through hydrogen bonding interactions (Vetere et al., 2002).

From the perspective of time efficiency and minimizing waste, the one-pot conversion of citronellal into menthol is a better approach (Cortés et al., 2011; Makiarvela et al., 2005). Bifunctional catalysts and the superacid solid catalysts act properly for both mechanisms. One-pot reactions catalyzed by Pt^- , Ru^- , and Ni^- -based catalysts were reported (Cortés et al., 2011).

Similar to other organic reaction mechanisms with transition metal catalysts, the supporting materials influence either the dispersion and stability of the active metal or the mass transfer of the reactant feed for conducting surface reactions. Table 3 lists the activity of some porous material-supported metal catalysts in the citronellal conversion. The interaction between the active metal and the support plays a role in controlling the surface reactivity, and furthermore, the conversion and selectivity. For example, when producing menthol on an MCM-41 support, the reactivity and selectivity of the active metals rank in the following order: $Ni > Pd > Ru > Ir$ (Makiarvela et al., 2005). The ratio of Bronsted to Lewis surface acidity governs the possible side reactions. This is also identified by the use of Ni-supported material on clay minerals (Fatimah et al., 2015; Fatimah et al., 2016).

From Table 3, it can be seen that although in general the higher the specific surface area of the catalyst, the higher the conversion, the catalytic conversion and selectivity in cyclization and hydrogenation is not only influenced by the specific surface area of the supports, but also by their interaction with the supported metal. Acidity of the supports provides the surface acidity for sufficiently promoting the cyclization step, while the presence of supported metal enhances the catalyst-reactant adsorption surface interaction upon formation of isopulegol, as well as the hydrogen transfer in hydrogenation (Imachi et al., 2007; Balu et al., 2010). The dominant silica content in the solid supports tends to promote Bronsted acid, while the presence of Al gives a combination of Bronsted and Lewis acidity. In addition, for the hydrogenation step, the study from Nie et al., 2006 showed an increasing Ni loading from the Ni/BEA

Table 3. Comparison on Activities of Some Metal-Supported Porous Materials in Citronellal Conversion

Catalyst	Metal content (%)	Surface area (m ² /g)	Surface acidity	Conversion (%)	Selectivity to isopulegol (%)	Selectivity to menthol (%)	Reference
ZnBr ₂ /C ₈ -HMS	2.6	1200		94	86	-	(Imachi et al., 2007)
Ni/MCM-41	15	659		96	8	74	(Nie et al., 2006)
Ni/Natural Zeolite	5	29	-	50	50	0	(Adilina et al., 2015)
Ru/H-MCM-41	10	522		96.4	2.2	46.6	(Vajglová et al., 2020)
Pd/Ga-SBA-15	1.92	799	65 mmol pyridine/g	>90	15	75	(Balu et al., 2010)
Pt/Al-MCM-41	2.02	905	199 mmol pyridine/g	95	15	60	(Balu et al., 2010)
Cu/Al-MCM-41	1.85	752	210 mmol pyridine/g	90	8	87	(Balu et al., 2010)
Zr/Pillared montmorillonite	5	97.5	1.05 mmol butylamine/g	89.8	98.5	-	(Fatimah et al., 2016)
Ru(Bpy)/Saponite	1.89	229.35	-	98.12	95.02	2.58	(Fatimah et al., 2015)

catalysts that leads to faster hydrogenation and selectivity to produce menthol in a one-pot conversion. Particularly, the hydrogenation rate was insignificantly influenced by the increasing particle size, for example, in the Ru-deposited material on MCM-41 (Vajglová et al., 2020), and Pt–Ga-MCM-41 (Balu et al., 2010). The nanoparticles formed from active metals demonstrated a highly stable catalytic activity, as represented by better reusability (Balu et al., 2010; Fatimah et al., 2019).

Heterogeneous catalysts suitable for the cyclization reaction of citronellal-enes must have strong Lewis acids and weak Bronsted acids (Chuah et al., 2001). The fast reaction rate of ene reactions in (+)-citronellal cyclization with a sulfate zirconium catalyst affects stereoselectivity. The result is a maximum stereoselectivity of 61%. However, high stereoselectivity (72%) was obtained from a zirconium hydrate catalyst. A ZrO₂ acid catalyst, which has a low surface area, is also active in cyclization. In addition, a high ene reaction rate can also be obtained when using a SiO₂-Al₂O₃ mixed catalyst with a maximum stereoselectivity of 72%. One of the factors determining the activity of the ZrO₂ and Al₂O₃ catalysts is the difference in their surface acidity type. ZrO₂ exhibits both Bronsted and Lewis acid sites, while the acidity of Al₂O₃ comes from the Lewis acid only (Makiavela, 2004).

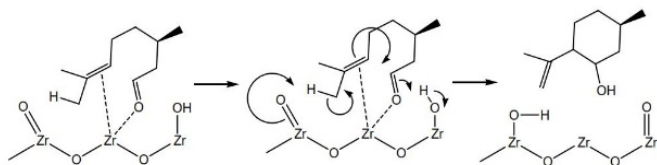


Figure 6. The Reaction Mechanism of Citronellal Cyclization to Isopulegol with Zirconium Hydroxide Catalyst (Chuah et al., 2001)

Other factors of the reaction system, such as the flow and batch systems, showed different results. The use of the extractive synthesis method has a major influence on physicochemical properties, especially on the level of Bronsted acidity, metal dispersion, and metal distribution in the material. In a batch reactor, Ru and Pt catalysts each support the acidity independently. This catalyst flow system does not depend on the acidity of the catalyst or the size of the metal particles, but it does de-

pends on the reaction kinetics, especially the mass transfer. This is evidenced by the stereoselectivity of menthol of 73% (Azkaar et al., 2019).

5. CLAY-BASED HETEROGENEOUS CATALYSTS

Clay minerals contain silica-alumina frameworks characterized as a layered structure with exchangeable cations that potentially can be replaced with metal or metal oxide. The modification of clay can be conducted based on the exchange of alkali or earth alkali (Na⁺, K⁺, Mg²⁺, Ca²⁺) cations with other metal cations, giving increasing porosity caused by an expansion of the interlayer distance (Banković et al., 2012; Barakan and Ag-hazadeh, 2019). Cations located in the interlayer space can be exchanged with organic and organometallic cations in solution or in solid conditions (Belver et al., 2012; Wang et al., 2016). Natively, clay minerals containing Bronsted acid and Lewis acid sites refer to the interlayer charges and the silica content within the structures. As the cation exchange is conducted with polyoxometal cations of transition metals, the formation of Lewis acid sites can be achieved instead of the enhancement of chemical interactions, such as hydrogen bonds, ion-dipole interactions, coordination bonds, and transfer forces or van der Waals forces. Previous studies have reported that tetraalkylammonium compounds can be easily introduced into the interlayer space, causing changes in pore structure and shifting of the interlayer distance (Mao et al., 2009; Nagendrappa, 2011). However, this thermal material is not stable at temperatures above 250°C. Incorporation of metal oxides as pillars increases Bronsted and Lewis acidity. In addition, this material can be used in redox or cycloaddition reactions as well as catalytic activity due to its high specific surface area (Cecilia et al., 2018).

According to Baloyi et al., 2018, the development of catalysts, with a focus on low cost, stability, reusability and an environmentally friendly aspect, and catalysts such as pillared clays, will lead to the discovery of effective solids as heterogeneous catalysts. In silica-alumina materials, clay-based catalysts exhibit a high surface area, and they can be modified and reused (Chmielarz et al., 2018; Kooli et al., 2016).

In previous studies, González et al., 2017 reported that montmorillonite had been pillared by Al₁₃⁷⁺ polycations, using concentrated solutions and clay mineral dispersions. The reaction is assisted by microwave radiation, producing a new

intercalation solid, and leading to an Al pillared solid after calcination at 500°C. The solids obtained show structural characteristics comparable to those of Al-PILC prepared from the classical method (Manos et al., 2001; Pinto et al., 2012).

Several modification schemes can be applied to identify a more active catalyst for the homogeneous distribution of metal or metal oxide catalysts in the clay structure. As an effort to preserve the specific surface area along with surface acidity, modified clay with a porous structure was also attempted, one of these being in the form of a porous clay heterostructure (PCH) (Kalmakhanova et al., 2019; Liu et al., 2007). Modification showed that the formation of metal oxides in the interlayer space of the smectite clay structure provides stability, and more importantly, maintains surface acidity in certain acid catalytic mechanisms (Cecilia et al., 2018; Panda, 2018; Radwan et al., 2009).

The results of the research by Chmielarz et al., 2018 reported that the BET surface area (SBET) was determined for calcined Ti-PILC and Ti-PCH. Ti-PILC calcination at 550°C produced samples with the highest surface area of 212 m²/g. At higher temperatures, partial collapse of the Ti-PILC pillar structure is possible. The Ti-PCH calcination at 600°C produced a material with a surface area of 573 m²/g, which is much higher than Ti-PILC.

In the study of Kooli et al., 2017, smectite polarized with various numbers of Al species was reported and characterized, and the further use of this precursor was successful in the synthesis of Al-PCH materials. As a result, a greater specific surface area value was achieved and varied from 740 to 850 m²/g with the acid site. The Al content in the pillared clay and the PCH derivatives influence the catalytic data due to the different strengths of the acid sites and textures.

High surface acidity and surface area are the main factors affecting the increase in catalytic activity. In addition, the advantages of using PCH, especially in maintaining surface acidity in many catalytic mechanisms, are mainly attributed to PCH (Zhou et al., 2013). The combination of metal oxides and PCH is also expected to provide mutually beneficial relationships for several desirable properties in the reaction, including catalyst activity and selectivity, referring to the presence of metals as the specificity of the active site (Cecilia et al., 2018; Chmielarz et al., 2018; Kooli et al., 2017).

Surfactants are another determining factor in PCH synthesis. The preparation of the H⁺-titanosilicate/dodecylamine (DDA)/tetraethylortho-silicate (TEOS) intercalation compound is rapidly hydrolyzed in water to form H⁺-titanosilicate pillared siloxane and calcined for 5 hours at 500°C to produce a mesoporous H⁺-titanosilicate. The results obtained show a basal distance of 4.16–4.32 nm, a uniform pore size of 2.8–3.4 nm, and a large surface area of 535–618 m²/g. These results suggest that the DDA molecule plays a decisive role in pore formation, as it acts as a base catalyst and as a micelle-like template during the hydrolysis of TEOS and contributes to the formation of solid silica pillars (Park et al., 2009). Therefore, the schematic of PCH formation is shown in Figure 7.

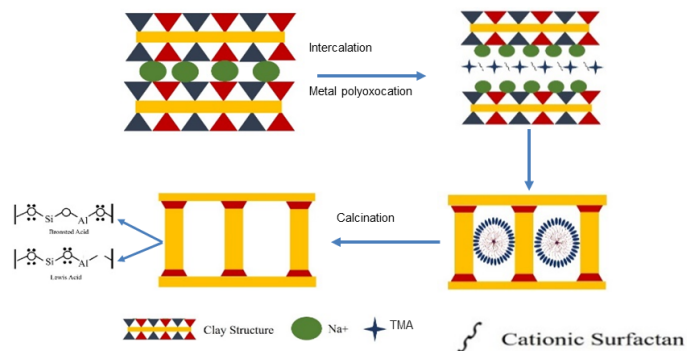


Figure 7. Schematic Representation of PCH Formation (Rubiyananto et al., 2019)

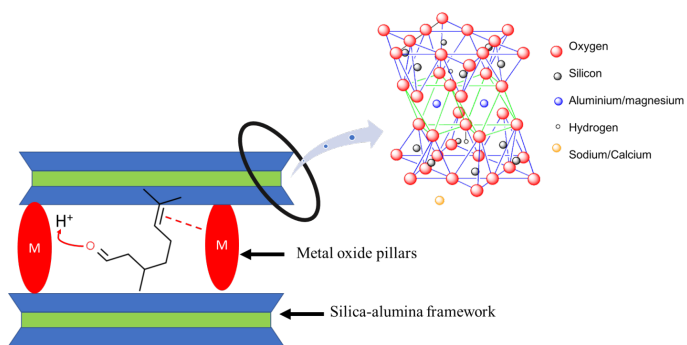


Figure 8. Schematic Representation of Citronellal Conversion by Clay-Supported Metal

The pillared clay can also act as a solid support for other metals or metal oxides, for example, TiO₂ dispersed in silica-pillared montmorillonite (TiO₂/SiO₂-montmorillonite). Previous work reported that the use of a TiO₂/SiO₂-montmorillonite catalyst played a significant role in increasing the total reaction conversion from 87.80% in the use of SiO₂-montmorillonite and from 85.38% using natural montmorillonite to 95.53% (Fatimah et al., 2008). The increase in total conversion and selectivity to isopulegol was related to the Lewis acidity of TiO₂/SiO₂-montmorillonite and the increase in the specific surface area of the material. However, it is possible that the specific surface acidity plays a greater role than the physicochemical character of the materials in this range. This means that the TiO₂ dispersion on the SiO₂-montmorillonite catalyst does not have a significant role in increasing the reaction rate. Changes in physicochemical properties of catalysts by the presence of titanium dispersion play a role in directing the mechanism so that it plays a significant role in the selectivity and catalytic activity. Figure 8 represents the mechanism of citronellal conversion using clay-supported metal/metal oxide.

The very simple inorganic material, montmorillonite, which is a natural acid clay, can effectively promote the synthesis of nitrogen-containing octahydroacridine, with 92% yield in one hour and at room temperature, ranging from aniline and cit-

ronellal, as well as the main components of several essential oils. The use of a solid acid catalyst gives a high selectivity to isopulegol compounds. Therefore, the use of solid acid catalysts can minimize waste and shows high potential for sustainability (Zaccheria et al., 2018).

The synthesis of Zr-montmorillonite in acetonitrile is used in the citronellal cyclization reaction. The presence and strength of Lewis acid catalyst Zr-montmorillonite plays a role in producing isopulegol 98% with stereoselectivity to (–)-isopulegol 90%. As some Lewis acids are used that are stronger than Ti^{4+}/Zr^{4+} , such as Al_2O_3 , SiO_2-TiO_2 and SiO_2-ZrO_2 , the stereoselectivity with respect to the (–)-isopulegol are 70, 62, and 62%, respectively. The type of Lewis acid carried on mesoporous materials, $ZnBr_2/SiO_2$, can produce (–)-isopulegol with a maximum stereoselectivity of 86% (Makiarvela, 2004).

Guidotti et al., 2000 suggested that the conversion of citronellal to isopulegol epoxide using a mesoporous titanium silicate catalyst (Ti-MCM-41) in one step at the same time resulted in 68% yield. The cyclization process of citronellal to isopulegol takes place in a toluene solvent for 6 hours, and then tertbutylhydroperoxide (TBHP) and acetonitrile are added to convert isopulegol to isopulegol epoxide for 18 hours at 76% and selectivity 90%. A catalyst consisting of nickel dispersed in zeolite (Ni/ZAB) was also reported to be effective for the conversion of citronellal oil to isopulegol from lemon grass oil, which reached a total conversion of 100% and a selectivity of 57% (Tursiloadi et al., 2015).

The significant role of specific surface area was summarized from the significant increasing citronellal conversion and selectivity toward isopulegol over Zn-dispersed-in-clay, via the formation of a porous clay heterostructure (Zn/PCH), according to (Rubiyanto et al., 2019). The physicochemical properties increase in line with the increase in catalytic activity and selectivity in the conversion of citronellal to isopulegol, compared to Zn/pillared clay (Zn/PCH). Zn/PCH showed a 98.9% conversion rate for the 3-hour reaction and 100% selectivity for isopulegol production, and showed good reusability.

Surface acidity enhancement was also reported for a combination of bimetals: nickel and zirconium in the form of nickel immobilized zirconia pillared saponite (Ni-Zr/SAP). Zr-pillared saponite (Zr/SAP) was prepared by microwave-assisted pillarization, and it was employed as the solid support of nickel by the impregnation method. The physicochemical characterization identification showed that zirconia was successfully distributed as pillars, and nickel was dispersed in the pillared material. Both modifications increased the specific surface area, pore volume and surface acidity as a result of the formation of pillars and homogeneous particle distribution. Compared to saponite and Zr/SAP, the Ni-Zr/SAP composite demonstrated a significant improvement in citronellal conversion and selectivity towards isopulegol. The presence of nickel plays a role in the one-pot conversion of isopulegol into menthol over a catalytic hydrogen transfer reaction. As nickel has specialization for hydrogenation mechanisms, Ni-Zr/SAP produced menthol in a significant selectivity (13%) (Fatimah et al.,

2016; Fatimah et al., 2015). It was reported that the selectivity in producing menthol was influenced by the reaction method, for which the microwave-assisted hydrogenation showed higher conversion and selectivity compared to the conventional reflux method, but for both methods, isomenthone as another hydrogenation product was identified.

The increasing quantity and distribution of surface acidity can be achieved by dispersion in a clay support via pillarization. Zirconium-pillared montmorillonite (Zr/MMT) demonstrated the increased surface acidity that was in line with the increased citronellal conversion into isopulegol, according to Fatimah et al., 2014. Moreover, the surface acidity enhancement was achieved by sulfation into the form of sulfated-Zr/MMT (S-Zr/MMT). The contribution of pillarization through increasing specific surface area by the higher basal spacing d_{001} of the structure, together with the formation of ZrO_2 pillars, were the factors identified for the catalytic activity. In addition, by the anchored sulphate functional groups on the surfaces, the super-acidity of the surface was created, reflected as the highest activity of 98.52% citronellal conversion obtained by S-Zr/MMT.

In a different form, the dispersed active metal catalyst of tris(bipyridine) ruthenium (II) into a saponite clay support ($Ru(Bpy)_3/Sap$) for the bifunctional conversion was also reported. The ($Ru(Bpy)_3/Sap$) exhibited activity in citronellal and citral conversions in catalytic hydrogen transfer under the microwave irradiation method. The hydrophobicity of the complex provides the possibility of acidity transfer as demonstrated by the activity in a non-solvent reaction system. The anchored metal complex in the support is remarkably maintained for 5 uses in its recycling activity (Fatimah et al., 2019).

Considering the role of surface acidity on the catalyst, hydrophobicity, and maintenance of catalyst performance in terms of reusability, the chosen heteropoly acid (HPA) catalysts in clay supports is hypothesized to give more effective catalytic mechanisms. The majority of catalytic applications of HPA are related to the stable and stronger acidity coming from the available Keggin HPAs heteropoly anions of the formula $[XM_{12}O_{40}]_n$, where X is the heteroatom (such as P^{5+} and Si^{4+}) and M is the addendum atom (such as Mo^{6+} and W^{6+}).

Tungsten (W) is a transition metal and has various catalytic applications in the form of tungsten sulfide, tungstic acid, polyoxotungstates (HPW) and polyoxometallics (POM). The advantages of tungsten, especially in its heterogeneous form, are its high Bronsted acidity, redox ability, thermal stability, and hydrophobicity (Nagendrappa, 2011; Telalović et al., 2010; Zhou et al., 2013).

HPWs possess stronger acidity than conventional solid acid catalysts such as zeolites, acidic metal oxides, and mineral acids. The acidity of concentrated aqueous and non-aqueous solutions of HPW is higher than that of H_2SO_4 and $HClO_4$ by about 1.5 or 0.3 units of the Hammett acidity function. The acid strength of Keggin HPWs decreases in the following order: $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiMo_{12}O_{40}$ (Alsalmeh et al., 2010). The superacidity characteristics of HPWs al-

low them to catalyze esterification activity of oleic acid with methanol at room temperature and to display a higher esterification activity compared to Amberlyst 35W resin (Alsalmeh et al., 2010; Nogueira et al., 2020). Similarly, the HPW exhibited a high activity of 1-propanol and 1,1-diacetates from a variety of aldehydes at room temperature (Heravi et al., 2006). The conclusions from many studies on HPW catalysis have demonstrated the usefulness of HPW, being more effective than ordinary protonic acids. Emphasis is placed on the optimization of HPW as a reusable catalyst with high performance to achieve the economic and technical advantages in applications, and one of various alternative methods is the immobilization of HPA onto porous material.

The study on immobilization of 12-tungstophosphoric acid (HPW) on the catalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ /mesoporous acid activated bentonite (AAB) was carried out. The results showed that the 2-propanol transformation increased substantially with the conversion, and the reaction selectivity also increased with increasing HPW concentration. In addition, the proposed catalyst increases the oxidation of 2-propanol to acetone and suppresses the dehydration of propanol to acid-catalyzed propylene. The catalytic activity increases the formation of acetone and decreases the activity of propene formation, which indicates that a catalyst with a high HPW concentration can function as an efficient catalyst for oxidation reactions (Rozić et al., 2011).

Immobilization of HPW and POT into supports such as polymers, silica, alumina, zeolites, and carbon materials not only increases the stability of the POT supported through covalent bonding, but also increases the spread of the POT active site into the support. At present, although tungsten based heterogeneous catalysts are used in industry with high efficiency for some reactions, regeneration of POM-based catalysts is generally difficult. Therefore, to encourage the use of W-based heteropoly acid catalysts, it is very important to develop catalytic systems that can be regenerated efficiently through catalyst heterogenization (Enferadi-Kerenkan et al., 2018). Silica supported $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW), which has high hydrophobicity, and which is the strongest heteropoly acid in the Keggin series, is an efficient, environmentally friendly heterogeneous catalyst for the liquid-phase isomerization of α -pinene and longifolene into their more valuable isomers—camphene and isolongifolene (da Silva Rocha et al., 2009). The environment friendly benefits of the catalyst can be derived from its ease of separation from the reaction system without neutralization, and it may be easily reused (Robles-Dutenhefner et al., 2001).

According to Cortés et al., 2011, an $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ catalyst was used to convert (+)-citronellal to (–)-isopulegol and (+)-neo-isopulegol as the main products with almost 100% conversion, with a total selectivity between 95 and 100%, and 80% are selective against (–)-isopulegol. The catalyst can be used repeatedly without decreasing activity. While the Pd- $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ catalyst is an efficient heterogeneous bifunctional catalyst for conversion in one process from (+)-citronellal to menthol with a conversion result of up to 92%, and 85% stere-

oselectivity for the desired product (menthol) (da Silva Rocha et al., 2007).

Meso/macroporous $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ nanocomposites with high specific surface area were prepared using cationic surfactants and monodispersed polystyrene (PS) as dual templates. The results of X-ray photoemission spectroscopic (XPS) measurements showed a high dispersity of Keggin-type heteropoly acids (HPA) on the silica matrix. There is an optimum value for the use of cationic surfactants and the right calcination temperature of the $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ meso/macroporous catalyst which leads to a very high specific surface area of $1,457.7 \text{ m}^2/\text{g}$ at a calcination temperature of 450°C (Yue et al., 2020).

In addition, several materials containing tungsten oxide (WO_3) were prepared and deposited on SiO_2 by the sol-gel method and the wet impregnation method. The tungsten oxide weight varies (1, 10, 25 and 40 wt%), namely W10, W25, and W40. The WO_3 - SiO_2 catalytic activity of these materials was tested in the intramolecular citronellal Prins cyclization reaction. The reaction conditions (temperature 70 – 90°C , amount of catalyst 1–10% catalyst density) had an effect on citronellal conversion and selectivity in producing isopulegol. The best results (90% isopulegol, 97% selectivity of isopulegol formation, 24 hours) were obtained using the IMP W25 catalyst (10 wt%, 50°C). It is possible to reuse the W25 catalyst twice without losing significant activity. The available materials indicate a suitable catalyst for citronellal cyclization (Vrbková et al., 2020).

In a study by Braga et al., 2012, it was reported that a catalyst based on 12-tungstophosphoric acid supported on mesoporous MCM-41 (2–40 wt%) was prepared and tested in citronellal cyclization. The characterization of the ingredients confirmed the Keggin anion treatment. These materials give rise to acidity that is related to the presence of Bronsted and hydrogen bond sites. The increase in HPW load is directly proportional to the number of Bronsted sites in the material. All the catalysts that were actively prepared in the citronellal cyclization formed the main stereoisomer (–)-isopulegol, but kinetic studies showed that 20% HPW/MCM-41 had the best performance with a conversion of about 96% and a selectivity of 65% for an hour reaction. This catalyst was reused four times with a low deactivation rate, keeping the selectivity almost the same. Thus, the successful application of HPW supported on MCM-41 for this acid-catalyzed cyclization is demonstrated, and detailed information on the stability of the catalyst as well as the kinetics of the reaction is provided.

6. FUTURE PERSPECTIVE

The combination of surface acidity and porosity of support with a metal catalyst plays a role in preserving heterogeneous acid catalysts in the citronellal conversion. From the perspective of green chemistry, some considerations are concluded. The one-pot citronellal conversion into menthol is preferable compared to two-step reactions, therefore the capability of catalysts for both cyclization and hydrogenation mechanisms is an important issue. The reusability of the catalyst that accommodates

its use in several cycles will contribute to minimizing waste and achieving a more economical process. The high-selective product, especially for a specified isomer is determined by the use of specific transition metal. The chemical and thermal stability of the catalyst is the significant feature, and in addition, the design of a stable catalyst based on low-cost material has a good chance of being developed. The modified clay with good porosity, such as in the porous clay heterostructure form, is hypothesized to be a good candidate for a low-cost catalyst support. From our literature review, we have determined that the combinations of clay-based materials with superacidity, such as a heteropoly acid, need to be explored and optimized.

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