

Benzyl Acetate: A Review on Synthetic Methods

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ABSTRACT

Synthetic methods of benzyl acetate using different catalysts such as strong acid cation exchange resin, Palladium, Benzyl trialkylammonium, Polyaniline, Sb-Pd-TiO₂, Pd,Sb/TiO₂, Bronsted acidic ionic liquid, H₂SO₄(NH₄)₂ Ce (PO₄)₂ .H₂O, SiW₁₂/SiO₂, Ni/SiO₂, (NH₄)₆{Mo₉O₃₂}.8H₂O, Micro/Meso - HZSM - 5, Lipase Immobilized, 1-methyl-3-(3-sulfopropyl) imidazolium tungstophosphate, salt / glycerol all these catalysts have been reviewed and studied. The catalysts that used in preparation of benzyl acetate improved the some properties such as yield, temperature and reaction time of benzyl acetate. These techniques benefit from simple procedures and minimal investment costs.

Keywords:

Esters, synthetic methods, catalysts, benzyl acetate

Introduction

In the culinary, cosmetic industries, and pharmaceutical, esters are compounds of significant economic value [1]. With applications in many different industries, benzyl acetate is one of the short-chain carboxylic acid esters of greatest importance. Its yearly output can reach 10,000 tons. Since this ester is found in plants like gardenia and jasmine, it can be acquired naturally. However, its direct purification and extraction are very difficult and expensive [2]. Although ester

synthesis using conventional chemical techniques is feasible, these techniques have many drawbacks, including high temperatures, the toxicity of the reagents used, low selectivity are used of corrosive catalysts, increasing the likelihood that byproducts will be produced that will prevent the target product from being purified. [3]. This crucial industrial process suffers from the use of volatile organic solvents in addition to these issues [4]. A quick, easy, and effective approach for aromatic esters synthesis is urgently needed in light of the

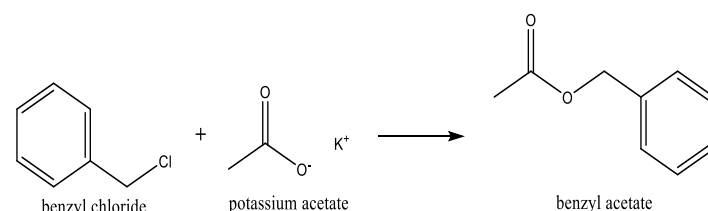
mounting ecological and economic challenges. [5,6]. There is an international initiative to replace conventional catalysts with eco-friendly catalysts in light of environmental regulations. The most fundamental and significant reaction in the synthesis of organic compounds is esterification. [7]. Since the intended products go through additional oxidation, the direct partial oxidation of ($\text{CH}_3 - \text{Ar}$) to their corresponding (ROH) or (RCHO) is frequently non selective as a result, these oxidation processes instead continue to produce more thermodynamically stable byproducts, such as benzoic acid from toluene. Therefore, creating more appealing procedures and effective catalysts lead to produce the needed chemicals as stable end products will be a significant issue in the future. [8]. In industrial production, benzyl acetate is also produced by homogeneous catalysis of materials benzyl butanol and acetic acid however, the dehydration and oxidization ability property of concentrated sulfuric acid results in a number of drawbacks, including numerous side reactions, difficult post-treatment, significant wastewater production, severe equipment corrosion, and significant environmental pressure. [9]. One of the most crucial steps in the synthesis of organic compounds is the acylation of aromatic and aliphatic alcohols, acid anhydrides can be used in acylation to shield (O-H groups) from oxidation and to couple processes or create esters, which have tremendous potential for use as perfumes, flavors, surfactants, and solvents. [10,11]. In the industrial setting, benzyl acetate is produced by esterifying glacial acetic acid (CH_3COOH) or acetic anhydride ($(\text{CH}_3\text{CO})_2\text{O}$) with benzyl alcohol in presence of (H_2SO_4). However, (H_2SO_4) can also result in a variety of undesirable byproducts, including dehydration, oxidation, sulfonation, and isomerization, it also severely corrodes equipment and pollutes the environment by releasing large amounts of wastewater effluent. [12]. One of the chemical procedures with economic significance to create benzyl acetate is the catalytic of benzyl acetic acid with benzyl alcohol (BA). [13]. Because enzymes are far more specialized,

selective, and active than traditional catalysts, they are frequently more practical for use as synthetic catalysts and in chemical synthesis. However, there are certain issues with using enzymes for commercial bio-catalysis, including their high production costs due to the fact that cells only produce them in small concentrations and the high cost of their extraction and purification. [14]. In this review article, the focus will be on the methods of preparing benzyl acetate, the use of different catalysts, and the effect of changing the catalyst on the results obtained in each method.

Discussion

1- Synthesis of benzyl acetate by strong acid cation exchange resin as a catalyst [15].

Benzyl acetate can be produced from (CH_3COOH) and ($\text{Ar} - \text{CH}_2\text{OH}$) using catalyst such as strong acid cation exchange resin. The ideal conditions were, respectively, the (25% wt./wt.) of above catalyst to acetic acid and the molar ratios of (CH_3COOH) and ($\text{Ar} - \text{CH}_2\text{OH}$) (2.0 : 2.25), reaction duration (10 hr), reaction temperature (373 K), and time (10 hr) 84.24 % of benzyl acetate was produced at maximal yield. When the catalyst was utilized again, it performed quite well. For instance, even after being used ten times, benzyl acetate still produced an 83.88 percent yield.

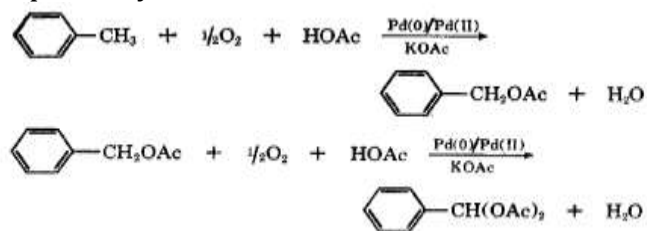


Scheme (1) chemical reaction of synthesis benzyl acetate by [strong acid cation exchange resin catalyst]

2- Synthesis of benzyl acetate from methyl benzene and a palladium-catalyzed [16].

The following ingredients were mixed at (373 K) for (9 hr) (482 gm , 8.03 mol) of (CH_3COOH), (107.8 gm , 1.11 mol) of potassium acetate, (92.1 gm , 1 mol) of toluene, (14.23 gm , 0.07 mol) of stannous acetate, (3.6 gm , 0.017 mol) of palladium (II) acetate, and 33.7 g

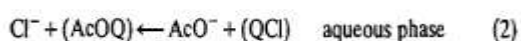
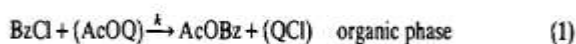
Distillation produced 66 grams of a liquid, bp (103-105 °C), following the typical work-up (20 mm). bp (222-223°C) (760 mm), benzaldehyde content of 4.5 gm (4.2%) and benzyl acetate content of 61.5 gm (41%) respectively.



Scheme (2) chemical reaction of synthesis benzyl acetate from methyl benzene and a palladium-catalyzed

3- Synthesis of benzyl acetate from phase transfer catalyzed acetate displacement of benzyl chloride [17].

Both the organic phase, benzyl chloride, and the aqueous phases, H₂O, AcONa, and PTC, were separately heated to the required degree. The aqueous layer in the conical flask was mixed with the organic layer. A tachometer was used to measure the stirring speed, and it was set once per hour to the desired value. At the proper intervals, the cap was opened, and just enough the mixture reaction was taken out to create the sample for the analysis.



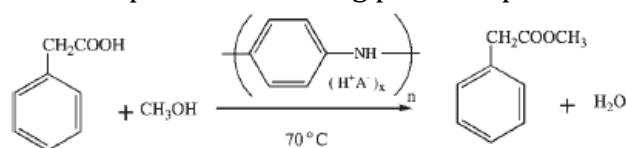
where (QCl) and (AcOQ) are ion pairs.

Scheme (3) chemical reaction of synthesis benzyl acetate from [phase transfer catalyzed acetate displacement of benzyl chloride].

4- Synthesis of benzyl acetate using polyaniline salts as catalyst [18].

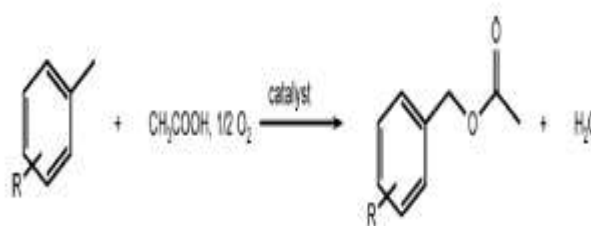
In a typical experiment, (200.5 mg) (20 % wt./wt.) of (PANI) salt powder was added to a (10 ml) round bottom flask along with (1 g) of phenyl acetic acid and (5 ml) of methanol with respect to phenyl acetic acid. For 24 hr, the reaction mixture at (243 K) was refluxed. To recovery the catalyst, the produced mixture was washed by methanol then filtered, Methanol was evaporated off as a solvent. The finished product was washed with distilled water after being treated with aqueous sodium

bi carbonate solution and ether. To create the product, anhydrous solid (Na₂SO₄) was mixed with ether solution, filtered, and then the ether operation is taking place evaporated.



Scheme (4) chemical reaction of synthesis [benzyl acetate using polyaniline salts catalyst].
5- Synthesis of benzyl acetate by highly efficient pd-sb-tio₂ catalysts for the vapor phase acetoxylation of toluene [19].

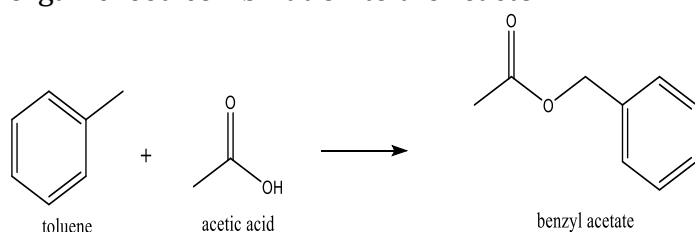
A continuous fixed-bed, vertical and tubular on-line, micro-catalytic steel reactor was used to conduct acetoxylation runs (length 112 mm, i.d. 6 mm). The reaction gases were provided from commercially available compressed gas cylinders and used without additional purification. The source of oxygen from air that used (20.6 percent O₂, in N₂), while argon (99.999 percent) was used as the diluent gas. Mass flow controllers were used to gauge the flows of three different gases. before each activity measurement, the reactor is loaded with about 1ml (ca. 0.80 g) with catalyst particles (0.45-0.65 mm size) and activated in an air flow of (27 ml/min) at (573 K) for (2 hr). A HPLC pump was used to deliver the toluene and acetic acid organic feed combination to the reactor. In a preheating zone on the reactor's top, the liquid reactant mixture was vaporized before it entered the reactor. Toluene, (CH₃COOH), O₂, and argon gas were the reactants, and their molar ratios were (1:4:3:16). The reaction was conducted at (483 K) and 2 bar pressure after the reactor was heated to reaction temperature and a mixture of air, argon, and vapourized liquid substrates was added.



Scheme (5) chemical reaction of synthesis benzyl acetate by [highly efficient pd-sb-tio2 catalyst]

6- Synthesis of benzyl acetate from the gas phase acetoxylation of toluene [20].

The stainless steel reactor with a fixed bed was used for the catalytic testing. The reactor is loaded with one milliliter of catalyst, and the reaction is carried out at a pressure of two bars. Prior to the activity testing, the catalyst was activated in place with airflow at (573 K) for 2 hr. A HPLC pump was used to deliver the toluene and acetic acid (CH_3COOH) organic feed combination to the reactor.

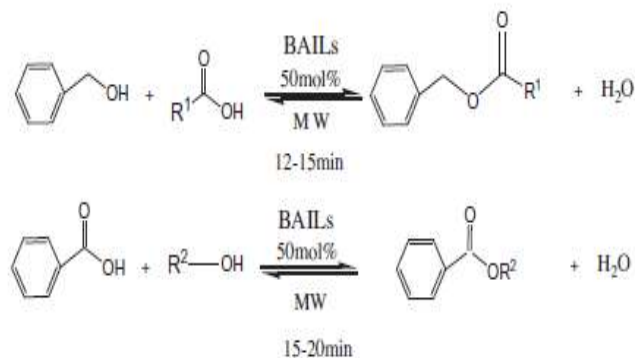


Scheme (6) chemical reaction of synthesis benzyl acetate from [the gas phase acetoxylation of toluene]

7- Synthesis of benzyl acetate by solvent-free synthesis in novel bronsted acidic ionic liquids under microwave irradiation [21].

In a 25 ml single-necked flask, the following ingredients were added: benzoic acid (1.77 mmol), aliphatic alcohol (1.77 mmol), and BAILs (0.89 mmol). The mixture of reaction was stirred at (298 K) until it reached a homogeneous phase before being put into the microwave reactor and heated for (20 min) at (353-383 K) or (383-393 K) while being mechanically stirred. When the reaction was finished, the mixture split into two phases, and the first layer show produced ester, it was easily separated by mixture decantation. In a subsequent run, the second layer made up of the BAILs was recycled. The created ionic liquid layer was subsequently dried under high vacuum for eight hours at (343 K) to eliminate water, leaving behind the BAILs (recovery 98.5 percent), which was recycled, after washing (3 times) with (20 ml) diethyl ether then stirring for (1.5-2 hr) at (298 K). Two times with a (NaOH, 2M) solution, then two times with water, the combined washing layers were cleaned, dried over MgSO_4 , and then filtered,

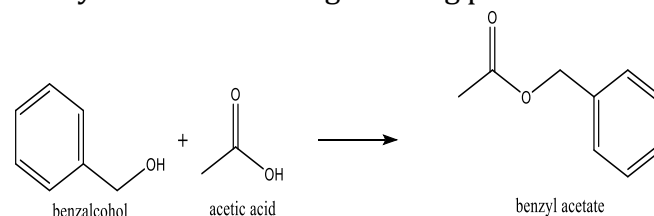
the filtrate was concentrated using reduced pressure distillation and rotary evaporation.



Scheme (7) chemical reaction of synthesis benzyl acetate by [solvent-free synthesis in novel bronsted acidic ionic liquids under microwave irradiation]

8- Synthesis of benzyl acetate by $(\text{NH}_4)_2 \text{Ce} (\text{PO}_4)_2$ as catalyst [22].

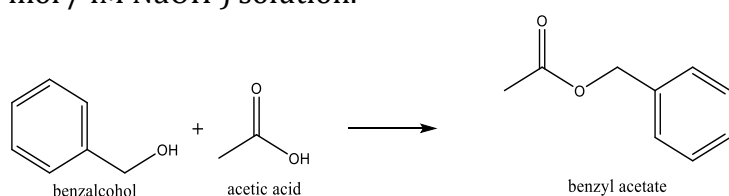
a combination of benzalcohol, glacial (CH_3COOH), and $\text{H}_2\text{SO}_4/(\text{NH}_4)_2 \text{Ce} (\text{PO}_4)_2$, stirring caused the water to reflux. The liquid pot's reaction temperature was maintained at 120°C . Following the completion of the reaction, the mixture of the reaction was filtered, and the remaining (CH_3COOH) was neutralized with suitable alkaline solution such as (NaOH) solution while phenolphthalein was used as an indicator. According to the quantity of acetic acid left over, the percentage of benzalcohol esterification was estimated. To determine the average result, each experiment was run three times. The mixture was then dried with anhydrous Na_2SO_4 after being rinsed with (H_2O), a dilute solution of (Na_2CO_3), and (H_2O). The goods were created by distilling the dry mixture with a little amount of (H_3BO_3), which caused benzalcohol to change into benzyl borate with a high boiling point.



Scheme (8) chemical reaction of synthesis benzyl acetate by [by $(\text{NH}_4)_2 \text{Ce} (\text{PO}_4)_2$ as catalyst]

9- Synthesis of benzyl acetate by ultrasound assisted heteropoly acid catalyst $\text{SiW}_{12} / \text{SiO}_2$ [23].

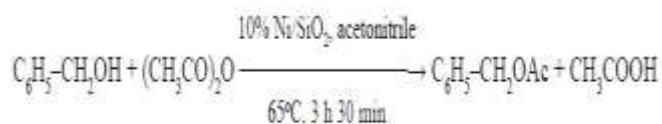
The cavitation-creating instrument, an ultrasonic horn, works at (10 kHz frequency), has a (2.1 cm) diameter. In 250 ml four-necked bottle the reactions were conducted, maintaining a constant volume of mixture reaction (100 ml) throughout. On the necks, a thermometer and a water separator were mounted. In a typical technique, toluene was dissolved in a mixture of solvents containing the suitable amount of (CH_3COOH) and (Ar. - CH_2OH), along with the appropriate amount of catalyst. The mixture was then cooked for two hours. To stir the mixes, a magnetic stirrer was offered. To calculate the amount of unconverted (CH_3COOH) as acid value, samples of the reaction mixture were removed at (20 min) intervals and titrated with (0.4 mol / 1M NaOH) solution.



Scheme (9) chemical reaction of synthesis benzyl acetate by [ultrasound assisted heteropoly acid catalyst $\text{SiW}_{12} / \text{SiO}_2$]

10- Synthesis of benzyl acetate by acylation of benzylic alcohol with catalytic system Ni/SiO_2 [24].

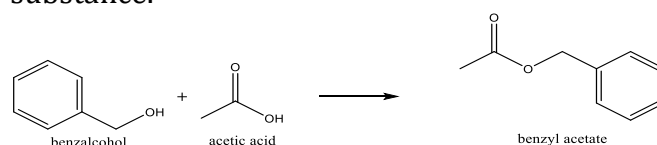
After preparing a solution containing (1 mmol) of benzyl alcohol, acetonitrile (10 ml) as solvent, (0.5 gm) of catalyst, (1.5 mmol) of acetic anhydride was slowly added at (338 K). Acetic anhydride was introduced to catalysts supported on silica for five minutes. The reaction mixture was continually agitated with a magnetic field. The reaction mixture was then extracted with ethyl acetate and quenched with deionized water. Anhydrous sodium sulphate was used to dry the organic layer, then rotavapour was used to evaporate the solvent to produce benzyl acetate as the crude product.



Scheme (10) chemical reaction of synthesis benzyl acetate by [acylation of benzylic alcohol with catalytic system Ni/SiO_2]

11- Synthesis of benzyl acetate catalyzed by anion exchange resin supported waugh-type $(\text{NH}_4)_6\{\text{MnMo}_9\text{O}_{32}\} \cdot 8\text{H}_2\text{O}$ [25].

In a three-necked flask equipped with a water knockout drum, reflux condensing tube, thermometer, and a constant pressure dropping funnel, a small amount of benzyl alcohol, glacial (CH_3COOH), then added methylbenzene as catalyst, the heating is then stopped, and the liquid of mixture reaction is poured out while the catalyst is recovered. The liquid of mixture reaction was washed with (Na_2CO_3) solution and saturated saline solution and distilled water and creates produced an ester layer. Then dried by anhydrous MgSO_4 and filtered to obtain product as crude, which is then subjected to reduced pressure distillation to collect (365–368 K / 1.33 kPa) cut fraction and produce benzyl acetate, a colorless and transparent substance.

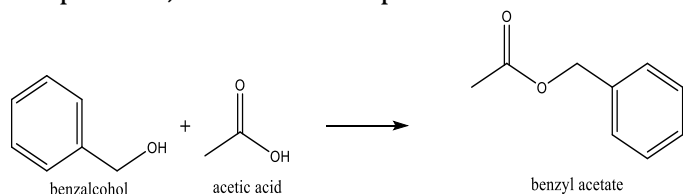


Scheme (11) chemical reaction of synthesis benzyl acetate by [anion exchange resin supported waugh-type $(\text{NH}_4)_6\{\text{MnMo}_9\text{O}_{32}\} \cdot 8\text{H}_2\text{O}$]

12- Synthesis of benzyl acetate by benzylation of acetic acid to benzyl acetate over highly active and reusable micro/meso-hzsm-5 [26].

The effectiveness of the synthesized catalysts using in the reaction of benzylation AA with BA. In (50 ml) two-necked glass flask, a reflux condenser to stop AA from escaping. By heated thermostatic oil bath kept the temperature accurate to within (0.5 K). The catalyst was then added to the flask after the addition of AA and BA, both weighted sequentially. The reaction was then carried out

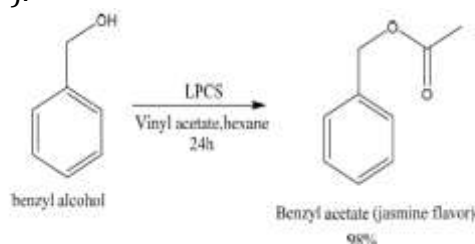
for 1-4 hours after the system had been heated to the necessary temperature (383–403 K), and ultimately the catalyst had been removed from the product, then collected product.



Scheme (12) chemical reaction of synthesis benzyl acetate by [benzylation of acetic acid to benzyl acetate over highly active and reusable micro/meso-hzsm-5]

13- Synthesis of benzyl acetate catalyzed by lipase immobilized in nontoxic [27].

the immobilized enzyme (0.005 g) was added to (0.021 ml) of (Ar. – CH₂OH) and (0.051 ml) of acyl donor (vinyl acetate, (CH₃COOH), (CH₃COOCH₂CH₃), and (CH₃COOCH₂CH₂CH₂CH₃) in (3 ml) of hexane solution. Then, aliquots were withdrawn after (14 hr).

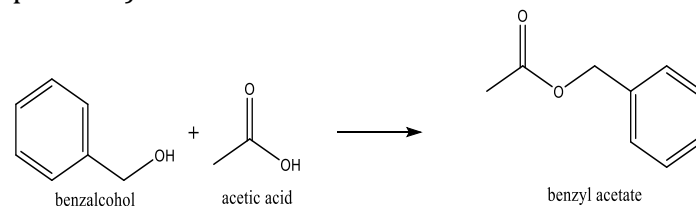


Scheme (13) chemical reaction of synthesis benzyl acetate by [lipase immobilized in nontoxic]

14- Synthesis of benzyl acetate by 1-methyl-3-(3-sulfopropyl)imidazolium tungstophosphate as a catalyst [28].

In place of (H₂SO₄) concentrate, the ideal reaction conditions were specified, including the reaction temperature of (383 K), the molar ratios of (acetic acid to benzyl alcohol) was (2.0:1.0) and (catalyst to Ar. – CH₂OH) was (0.2%). (95.52 percent) was the yield of benzyl acetate, while the yield after

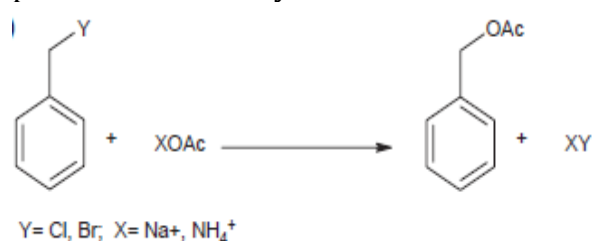
using the catalyst five times was (84.15 percent).



Scheme (14) chemical reaction of synthesis benzyl acetate by [1-methyl-3-(3-sulfopropyl)imidazolium tungstophosphate catalyst]

15- Synthesis of Benzyl Acetate by glycerol derivatives as green reaction mediums [29].

In a typical nucleophilic substitution method, 5 mL of solvent was combined with (0.71 mmol) of benzyl halide and the corresponding quantity of salt (0.78 mmol). then heated reaction mixture in an oil bath to the necessary temperature (353 K). The mixes were allowed to cool after the reactions finished running for an hour. After cooling, the product was extracted using (2 mL) of petroleum ether to separate it. Under reduced pressure, the organic phase was condensed to determine the product yield, Gas chromatography (GC) was used to examine the final crude using an HP-1 column. In order to conduct the extraction tests, (6 mL) of each solvent were combined with (6 mL) of petroleum ether and (0.55 g) of benzyl acetate. Following the evaporation of the extracting solvent at reduced pressure, the product extraction yield was determined.



Scheme (14) chemical reaction of synthesis benzyl acetate by [glycerol derivatives as green reaction mediums]

Table 1. Show some properties of different synthetic methods

No.	Yield %	Type of reaction	T / °C	Catalyst solvent or	Time	Other
1	84.23	Stirred	100 °C	strong acid cation exchange resin	10 hr.	
2	41	Stirred	100 °C	Palladium	9 hr.	
3	80	Oil bath reflux stirring speed	60 °C	Benzyl trialkylammonium	5 hr.	
4	91	Reflux	70 °C	Polyaniline	24 hr.	
5	100	Continous fixed – bed vertical and tubular online micro catalytic steel	300 °C	Sb-Pd-TiO ₂	2 hr.	Gaseous reaction ,
6	90	Fixed bed stainless steel reactor , HPLC pump	210 °C	Pd,Sb/TiO ₂	2 hr.	Gaseous reaction ,
7	95.4	Microwave reactor and irradiated	110 °C	Bronsted acidic ionic liquid	20 min.	
8	97.9	Reflux	120 °C	H ₂ SO ₄ (NH ₄) ₂ Ce (PO ₄) ₂ .H ₂ O	17 min.	
9	95	Sonochemical reactor	120 °C	SiW ₁₂ /SiO ₂	2 hr.	
10	97	Stirred	65 °C	Ni/SiO ₂	3 hr.	
11	87.4	Reflux condensing tube	95 °C	(NH ₄) ₆ {Mo ₉ O ₃₂ }.8 H ₂ O		
12	94	Reflux	110 °C	Micro/Meso HZSM - 5	60 min	
13	98	Stirred	65 °C	Lipase Immobilized	24 hr.	
14	95.52	Stirred	110 °C	1-methyl-3-(3-sulfopropyl) imidazolium tungstophosphate	5 hr.	
15	94	Stirred	80 °C	salt / glycerol	1 hr.	

Conclusion

From the above and the study of methods of preparation of benzyl acetate with different catalysts, the best catalysts was Sb-Pd-TiO₂ of maximum yield to produced benzyl acetate, according to the discussion and review above (100 percent). However, it is not

regarded as a promising option for the synthesis of benzyl acetate due to the high cost of power needs. H₂SO₄, NH₄, CE, PO₄ given yield to produced benzyl acetate (97.7 percent), which is asymptotic to the first technique, H₂O is an equally effective catalyst, but the difference is that it requires less energy and

takes less time. It was discovered that the $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ was proved to behave as an excellent heterogeneous catalyst in the synthesis of benzyl acetate, under the optimal reaction conditions, The ammonium cerium phosphate catalyst ($\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) had potential for industrial application since it was not only feasible and simple in synthesis technics, but also had good catalysis activity for the synthesis of benzyl acetate.

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