# Synthesis Of Ibuprofen Using Nano- Preyssler As A Green And Environmentally Friendly Catalyst

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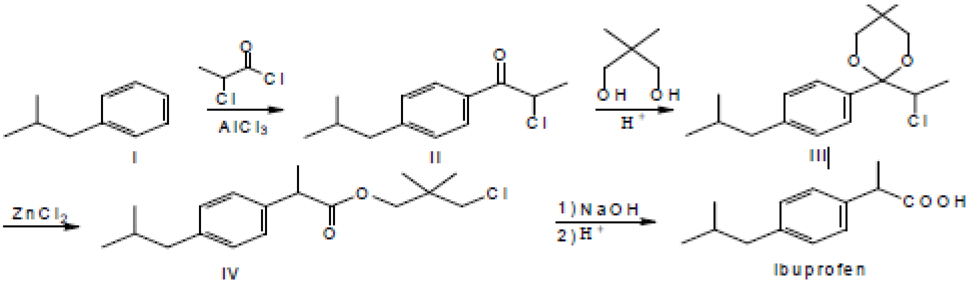
## ABSTRACT

Pollution and other environmental problems have become a threat to humanity's future as a result of the massive rise of the chemical, metallurgical, pharmaceutical, and other industries in the twentieth and twenty-first centuries. People did not pay much attention to global environmental problems until the middle of the twentieth century. Since the second half of the twentieth century, there have only been a few international attempts to modify this. We describe a novel catalytic technique for producing ibuprofen that use Silica-Supported Preyssler Nanoparticles (SPNPs) as an efficient, reusable, and environmentally friendly heterogeneous inorganic catalyst. The catalyst can be reused, and the method is simple and generates high yields. Ibuprofen is manufactured in three steps using standard reagents. However, the results demonstrate that the Silica-Supported Preyssler Nanoparticles catalyst produces the highest yield. In comparison to mineral acids such as H2SO4, the Silica-Supported Preyssler Nanoparticles catalyst is more active, selective, and has fewer side reactions. This polyanion is significant due to its strong thermal and hydrolytic stability across a wide pH range.

## INTRODUCTION

“Ibuprofen, also known as 2-(4-isobutylphenyl) propionic acid, which is a traditional nonsteroidal anti-inflammatory drug belongs to arylpropionic acid family. In 1986, Laska et al. (1986) studied the basic pharmacokinetic properties of ibuprofen and they concluded that the proposition increased ibuprofen serum levels lead to increased analgesia. Ibuprofen is widely employed for its analgesic, anti-inflammatory and antipyretic properties. Ibuprofen is available under prescription, primarily for the treatment of inflammatory and painful disorders (Manriquemoreno et al., 2016) including rheumatoid arthritis, ankylosing spondylitis, osteoarthritis, acute gouty arthritis and soft tissue injuries and so on".

The Friedel-Crafts acyl reaction involving isobutyl benzene and 2-chloropropionyl chloride was the starting point for the ary-1,2-translocation rearrangement method. To safeguard the carbonyl structure in 2-chloro-1-(4-isobutylphenyl) propan-1-one, a ketal reaction was performed between it and neopentyl glycol. The detailed process of creating something is shown below:



*"Figure 1: The technology roadmap of ary-1, 2-translocation rearrangement"*

The purpose of catalytic chemistry is to achieve the best possible synthesis in terms of catalytic activity, selectivity, atom-efficiency, and step-efficiency (Shimizu, 2014). The catalytic carbonylation method is simpler to employ and consumes more atoms than the ary-1, 2-translocation rearrangement. However, there are still issues, such as the high cost of the catalyst and the method's stringent working parameters, which make it difficult to spread its use. The majority of ibuprofen manufacturers in India and China adopt ary-1,2-translocation rearrangement. Because the catalyst is less expensive and produces less waste, the ary-1,2-translocation rearrangement is viewed as a good strategy to save cost and protect the environment.

"The process of ary-1, 2-translocation rearrangement involves four chemical reactions (Wang, 2014): Friedel- Crafts acyl reaction, ketal reaction, catalytic rearrangement reaction and hydrolysis reaction, and the ketal reaction is the key step. Ketal reaction is a heterogeneous reversible catalytic reaction that the conversion and rate of the reaction have serious impact on the production efficiency and yield of ibuprofen".

"The name ibuprofen originally came from the name is obutylpropanoicphenolic acid, but this nomenclature has not been used for many years and, in fact, virtually all chemists today are unfamiliar with it. Fortunately, however, the name is still a reasonably good match for the currently accepted name 2-(4-isobutylphenyl)propanoic acid. Ibuprofen ((+/−)2-(4-isobutylphenyl)propionic acid, Figure 1is one of the most commonly used anti-inflammatory agents. It is considered to be the prototype for the family of synthetic 2-arylpropionic acids, profens, a subclass of the nonsteroidal anti-inflammatory drugs (NSAIDs). In recent years, the profens have come to dominate this therapeutic class. Ibuprofen, for example, is used to treat arthritis, muscular strain, cephalalgia, and so forth".

The profens have a non-symmetrical carbon core that is linked to a carboxylic acid, a methyl group, and an aryl group with various structures. Figure 1 depicts some of the available profen drugs: (a) ibuprofen, (b) naproxen, (c) ketoprofen, and (d) flurbiprofen (d). Ibuprofen is available without a prescription, while naproxen was among the top 10 medications sold worldwide in 1989. Ibuprofen is utilized to treat headaches, backaches, menstruation pain, tooth pain, neuralgia, rheumatic pain, muscle discomfort, migraines, cold and flu symptoms, and arthritis. NSAIDs primarily exert their pharmacological and toxicological effects by inhibiting the binding of arachidonic acid to the cyclooxygenase component of prostaglandin synthase. This reduces prostaglandin synthesis. In a variety of acid-catalyzed processes, heteropolyacids (HPAs) have been utilized as useful and adaptable acid catalysts throughout the past two decades. Heteropolyacids are significantly more active than inorganic and organic acids, and their molar catalytic activity is between 100 and 1,000 times that of H2SO4.

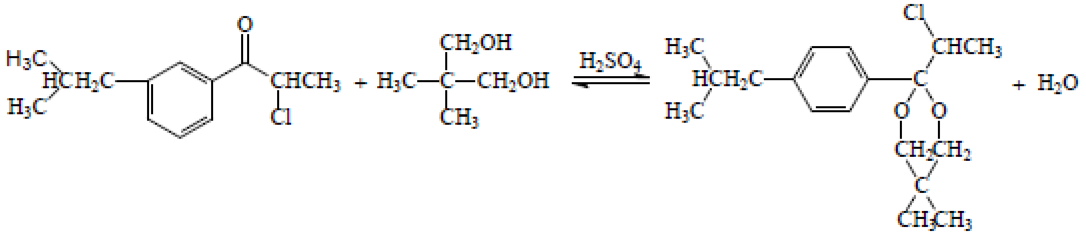
You can also use them sparingly. The most intriguing area of research right now is how to create and characterize catalysts with reduced dimensions. We know that as a particle's size decreases, the number of atoms on its surface increases, and hence activity increases. Nanometer-sized particles may have unique features that can be employed in a variety of ways due to quantum size effects. A Preyssler acid is a highly acidic catalyst from the heteropolyacid family that works effectively as a catalyst in acid-catalyzed processes.

*Synthesis of Ibuprofen* ***(6)***

"To a solution of ethyl-2- (4-isobutylphenyl) propanoate (1 g, 4.27mmol) in 6mL of CH3OH a solution of KOH was added (479mg, 8.55mmol) in 5mL of H2O. The resultant solution was stirred at room temperature for 4 h. Methanol was removed under reduced pressure and the resulting solution was extracted with ethyl acetate and the organic extracts were washed withH2O, dried over anhydrous Na2SO4, and concentrated under reduced pressure to give compound **6**. M.P (∘C) 130-133, IR (KBr, cm−1): 3100, 2920, 2870, 1716, 1408, 1419, 1321, 1230, 1184, 935, 779, 668, 583. 1H NMR (400MHz, CDCl3) $\delta$H 7.15 (d, $J$ = 8.1Hz, 2H), 7.02 (d, *J* = 8.1Hz, 2H), 3.64 (q, *J* = 7.2Hz, 1H), 2.37 (d, *J* = 7.1Hz, 2H), 1.75 (m, 1H), 1.43 (d, *J* = 7.1Hz, 3H), 0.82 (d, *J* = 6.6Hz, 6H).13CNMR(100MHz,CDCl3): $\delta$c 22.81, 22.82, 29.07, 42.64, 44.50, 128.80, 128.93, 128.95, 132.22, 140.23, 181.26. Anal. Calcd. for C13H18O2: C, 75.69; H, 8.80%. Found: C, 75.61; H, 8.70%. HRMS (EI) Calcd. for C26H25FN4O6 [M]+, 206.1600, Found 206.1009".

## Analysis and solution

Neopentyl glycol and the product of the Friedel-Crafts acyl reaction, 2-chloro-1-(4-isobutylphenyl) propan-1-one, are used as raw materials in the ketal reaction that produces ibuprofen (chlorine ketone). As a catalyst, sulfuric acid is used to change the carbonyl group, and petroleum ether is used to carry out the reaction. These are the reaction equations:



Because it is so heavy, sulfuric acid sinks to the bottom of the reaction solution as the catalyst for the ketal reaction. It will weaken the reaction occurring in the top layer of the reaction solution between chlorine ketone and neopentyl glycol. Furthermore, the acidic environment will convert the ketal product to astaticism, resulting in reversible hydrolysis. Reverse reactions have a significant impact on conversion and the time required to attain equilibrium.

Two factors are critical to resolving these issues. To speed up the reaction, the catalyst-reactant mixture must be strengthened, and water, a byproduct, must be eliminated from the system to prevent it from flowing backwards. To get rid of water, consider the separation rate and the amount of free water carrier.

## LITERATURE REVIEW

Kharissova, O. V., Kharisov, B. I  et al,(2019) Modern developments in the environmentally friendly synthesis and production of inorganic, organic, and coordination compounds, materials, nanomaterials, hybrids, and nanocomposites are highlighted. The focus of green chemistry is on synthesis techniques that correspond to its 12 guiding principles. This increases the sustainability of chemical processes by saving energy and making reagents and end products less damaging to the environment and human health. It also reduces global warming risk and makes better use of natural resources and agricultural waste. Both well-known chemical compounds and wholly unique materials have been created using environmentally friendly approaches. Various nanosized materials and composites, such as metal and nonmetal nanoparticles, oxides and salts, aerogels, and quantum dots, can be produced by environmentally friendly methods. Simultaneously, conventional materials such as cement, ceramics, adsorbents, polymers, bioplastics, and biocomposites may be enhanced or generated from greener techniques. Several non-polluting physical techniques, such as microwave heating, ultrasound-assisted and hydrothermal procedures, and ball milling, are crucial for greener synthesis. These approaches are frequently employed in conjunction with natural precursors. Techniques such as solventless synthesis and biosynthesis are also very essential. Ionic liquids, plant extracts, fungi, yeasts, bacteria, and viruses are also discussed as non-hazardous solvents in the context of manufacturing materials. Scaling up green processes is discussed in terms of availability, need, and economics.

Jia, H., Du, D(2017) The ketal reaction is a critical step in the production of ibuprofen. The mechanism of the reaction was investigated in order to boost the rate of conversion. To find the best mixing method, the researchers examined mechanical stir, forced external circulation, and a combination of the two. According to the findings, the combination technique is preferable for mass transfer. Combining reactive and azeotropic distillation resulted in the elimination of water, increasing the efficiency of the reaction. The time it takes for the ketal reaction to occur has been reduced from more than 22 hours to less than 8 hours after the equipment was improved and the best way to run it was discovered. The upgraded ketal technology has been applied to industrial efficiency and proven to be beneficial to the bottom lines of two organizations.

Ji, H. F. (2014) “Green sustainable chemistry (GSC) is, in a word, chemistry and chemical technology for environmentally friendly products and processes. Green chemistry uses highly efficient and environmental benign synthetic procedures to deliver life saving medicines, accelerating guide optimization processes in drug discovery, with reduced needless environmental impact. HPAs have several advantages as catalysts which make them economically and environmentally attractive. Basic characteristics of heteropolyacids as green catalysts are overviewed, focusing on the various reaction fields in which the heteropolyacid catalysts function as acid. This research describes an alternative and simple procedure for the synthesis of Ibuprofen using SilicaSupported Preyssler Nanoparticles (H14[NaP5 W30O110]/SiO2 ), (SPNPs), as an eco-friendly, inexpensive and efficient catalyst. High yields, simplicity of operation and easy work-up procedure are some advantages of this protocol. Silica-Supported Preyssler Nanoparticles (H14[NaP5 W30O110]/SiO2 ), (SPNPs) offer the advantages of a higher hydrolytic and thermal stability. The salient features of Preyssler's anion are availability, non-toxicity and reusability".

Bamoharram, F. F., Heravi, M. M(2006). This polyanion is significant due to its high thermal and hydrolytic stability over a wide pH range. As a result, many catalytic reactions can be modified without losing their structure or function. H14-P5 produced the most esters of any Preyssler catalyst and sulfuric acid combination tested. The statistics also reveal that the molar ratio, reaction duration, temperature, and kind of alcohol all play a role. Without losing structure or activity, the Preyssler catalyst can be recovered and reused in both homogeneous and heterogeneous environments. Finally, this approach is useful for those who require solid catalysts with high acid strength, thermal stability, and the capacity to function across a wide pH range. It is simple to set up and execute the tests.

Heravi, M. M., Sadjadi, S (2009) By mixing anthranilic acid, orthoester, and substituted anilines in the presence of silica-supported Preyssler nanoparticles, researchers have reported a new and efficient method for producing 4(3H)-quinazolinones. When compared to other reported catalysts, the catalyst performs admirably. One of the nicest things about this catalyst is that it must be separated from the reaction mixture and can be used important times. There are numerous reagents that can be employed to create 4(3H)-quinazolinone derivatives, according to the literature. However, many of these methods have flaws, such as several stages, long reaction durations, expensive reagents, harsh environments, low product yields, reusing a lot of side products, and making it difficult to recover and reuse the catalysts. Cleaner and more efficient chemical synthesis is critical from both an economic and environmental standpoint. This suggests that further research is needed to develop low-cost, environmentally friendly chemical manufacturing ways.

Gharib, A., Pesyan, N. N (2014) "This paper describes an alternative and simple procedure for the synthesis of Ibuprofen using Silica-Supported Preyssler Nanoparticles (H14[NaP5W30O110]/SiO2) (SPNPs), as an eco-friendly, inexpensive, and efficient catalyst. High yields, simplicity of operation, and easy work-up procedure are some advantages of this protocol. Silica-Supported Preyssler Nanoparticles (H14[NaP5W30O110]/SiO2) (SPNPs) offer the advantages of a higher hydrolytic and thermal stability. The salient features of Preyssler's anion are availability, nontoxicity and reusability. We believe this methodology can find usefulness in organic synthesis. The advantages of this method are reusability of the catalyst, easy work-up procedure, and high yields. The Ibuprofen synthesis is carried out in three steps with usual reagents. However, the results show that Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) catalyst gives the highest yield. Compared with mineral acids, such as $H_2SO_4$, Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) catalyst is more active and shows a higher selectivity and minimized side reactions. Important features of this polyanion are high thermal and hydrolytic stability throughout a wide pH range".

Alimadadi, B., M Heravi, M (2016) Green chemistry is the key developing field providing us with a promising path for the future technologies. It also carries out chemical processes in a way that significantly reduces, or eliminates, all the hazardous substances. In recent years, using water in chemical reactions has been considered as a desirable, safe, inexpensive, and environmentally benign solvent rather than organic solvents.

## General synthesis methods

### Physical and chemical methods

"Physical methods such as mechanosynthesis, microwave-assisted and hydro(solvo)thermal reactions (and their combinations), ultrasound-assisted processes, and UV-irradiation of the reaction system, among others, are being investigated as ways to meet the green chemistry requirements of avoiding hazardous solvents, reducing pollution, and speeding up the synthesis process. Some of these methods are less common than others. Magnetic field-assisted synthesis, for example, is rarely used".

### Ball milling

Ball milling is a type of mechanochemical (tribochemical) synthesis that is often used in organic chemistry. It is also often used in solid-state inorganic processes. By using ball milling, we can use less energy and stop using dangerous chemicals and solvents. Both of these reactions, and the ones that MW helps with, happen at room temperature and don't need any solvents. Ball milling is regarded as a green chemistry instrument because it is simple and does not harm the environment. Even though it has a lot of potential, chemists don't use it very often.

### Microwave irradiation

This is a green source of heat based on conduction and dipolar polarization that can be used in both organic and inorganic synthesis. Several organic compounds have been synthesized utilizing this low-cost, simple, quick, and clean technique, which has become a staple tool in synthetic chemistry and has made a significant difference in organic synthesis. MW energy is non-ionizing radiation, which means it has no effect on how molecules are assembled. A substance's MW coupling is determined by its dielectric constant. As a result, N,N-dimethylformamide (DMF), methanol, acetone, and water are rapidly heated by MW irradiation, but not CCl4, toluene, or aliphatic hydrocarbons. Electromagnetic energy is converted into heat, which causes molecules to interact with one another. Because MW irradiation and reaction components work in tandem, just a little amount of energy is required to heat it up, and the process is not extended to the furnace material. As a result, the temperature profiles of conventionally heated simples and MW-heated simples differ (in the MW case, the interior is hotter and the surface is cooler).

### Photocatalysis

“Photochemical reactions under UV-irradiation are considered as green chemistry interactions and are based on the electronic excitation, which influences the chemical reactivity of reagents in organic synthesis. A recent review on photocatalysis describes generation of singlet oxygen and its role in the photo-oxygenation (incorporation of molecular oxygen into molecules), combination of photochemical processes with enzyme catalysis, application of continuous flows or microreactors for their optimization. Some examples of such reactions are the synthesis of N-containing heterocycles by photo-oxidation of furan derivatives, asymmetric oxidations catalysed with enzymes, and preparation of several F-organic compounds by photocatalysed trifluoromethylation of aromatics”.

### Hydro(solvo)thermal synthesis

Solution-reaction-based methods are used to make compounds, crystallize them, and make single crystals and polycrystals in water or organic solvents at high pressures (often up to 10 bar) and temperatures (usually up to 300°C). The hydro(solvo)thermal process uses an autoclave, which is a steel cylinder with thick walls and protective inserts made of Teflon, platinum, titanium, quartz, gold, and other materials. The autoclave has water as a solvent and precursors that are suspended in the water. Over the last 20 years, a piece of equipment known as "microwave-hydrothermal treatment" has seen extensive application in laboratories. The fundamental advantage of the hydrothermal method is that it can produce crystalline phases that are unstable at the target compound's melting point. The biggest disadvantage is that expensive equipment is required. Changes in pressure, temperature, solvent, reaction time, or precursor ratio can all be utilized to alter the form and crystallinity of the materials made. People believe that hydrothermal reactions in water are better for green chemistry since they are more environmentally friendly. These reactions are used to create a variety of materials. This method uses the fewest quantity of reactants and frequently delivers greater product yields. It is notably useful for creating powders, films, and one- to three-dimensional nanocrystals with the desired shape and size.

### Ultrasound-assisted (sonochemical) synthesis

Because cavitation only occurs in liquids, ultrasound-assisted (sonochemical) synthesis is exclusively a solution-based approach. It operates on the basis of the acoustic cavitation phenomena, in which bubbles in a liquid build and explode when they break, resulting in local pressures of 1000 atm and temperatures of 5000 K. This has no effect on the vibrational energy of the bonds. Free radicals and H2O2 can develop in these conditions, which can initiate or accelerate chemical reactions. As a result of these encounters, there may be significant materials in the chemical composition of a surface, how it interacts, and how it appears from the outside (often increasing its surface area). Sonochemical reactions can occur in liquid systems, at the interfaces of solids and liquids, and between liquids and liquids. Some of these reactions are beneficial to the environment, such as the breakdown of halogenated aromatics. Classic contributions to the field of "green chemistry" include ultrasound-mediated chemical synthesis and the production of functional materials. They do not require a lot of energy or hazardous chemicals, and the cost of equipment is also modest for a simple ultrasonic cleaning bath (20-40 kHz), with the exception of high-power ultrasonic horns.

## Results and discussion

### Characterization results

“We investigated the performance and capability of sodium-30-tungstopentaphosphate, also known as Preyssler's anion, for highly selective and efficient esterification of salicylic acid with some aliphatic and benzylic alcohols in the presence of various forms of Preyssler catalyst, namely pure, mixed addendum, and silica-supported. The results of comparing supported Preyssler HPA to non-supported Preyssler HPA reveal that the supported polyacid is always less active than the non-supported one. So it would be extremely fascinating to see what occurs in this esterification reaction when the nano-SiO2-supported Preyssler HPA is utilized. We discovered that the esterification reaction in an organic solvent works better with the nano-SiO2-supported Preyssler catalyst than with the SiO2-supported Preyssler catalyst. Silica nanostructures were obtained using the sol-gel technique. All of the circumstances are shown in the experimental section. Nanosized SiO2 with a BET surface area of 287 m2/g, a pore volume of 0.28 cm3/g, and an average pore size of 0.25 nm was obtained".

The BET surface area, pore volume, and average pore size after HPA impregnation were 201 m2/g, 0.10 cm3/g, and 0.21 nm, respectively. The optimal loading was 30%. Both the BET surface area and pore volume decreased, indicating that the nanosized silica pores are filling up and the supporting HPA is blocking some of the support pores.

The nanostructures created were studied using TEM, as illustrated in Fig. 1. This image has 40 nm spheres. SiO2 is crystalline, as confirmed by the XRD pattern of nano-SiO2, which revealed strong peaks in the 7o to 36o range. The absence of an XRD peak centered at 2 angle 22o, which is characteristic for amorphous SiO2, also confirmed the crystallinity. The spherical products' forms demonstrate that SiO2 has a specific structure.

"IR spectroscopy showed that the SiO2 nanoparticles have the heteropolyacid H14[NaP5W30O110]. This is shown in Fig. 2. The terminal oxygen's asymmetric stretching frequency is 960 cm–1, and the P–O asymmetric stretching frequency is between 1080 and 1165 cm–1. An anion with C5v symmetry would make sense for the strong P–O bands at 960, 1080, and 1165 cm–1. These bands show that H14[NaP5W30O110] is still in the nano particles of HPA/SiO2.".

"In addition, the protonated water band of H14[NaP5W30O110] also remained noticeable in the nanoparticles at 1730 cm–1. It could be confirmed that the heteropolyacid H14[NaP5W30O110] was successfully immobilized within the SiO2 nanoparticles since the heteropolyacid does not react with SiO2 or with water, but it can remain in the silica nanoparticles without appreciable change of the structure".

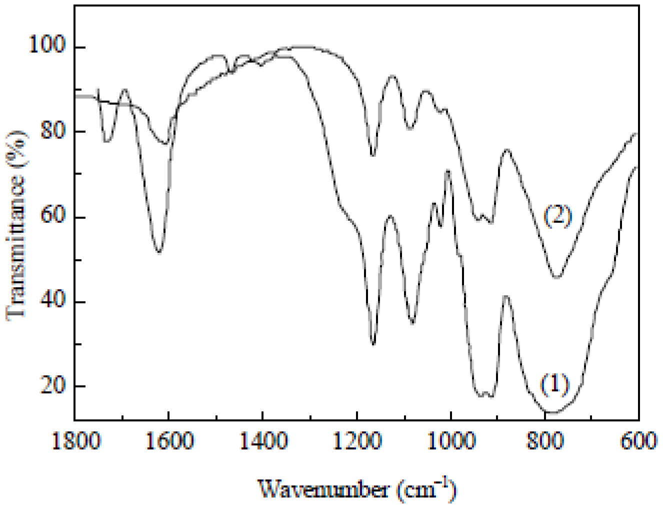


**Fig. 2.** IR spectra of Preyssler heteropolyacid in bulk form (1) and nano form (2).

## Catalytic activity

To test the catalytic activity of a nano-SiO2-supported Preyssler catalyst for the esterification of salicylic acid, the reaction was tuned for esterification with 1-pentanol. The researchers looked at the effects of variables like the type of solvent, the amount of catalyst, the temperature, the loading percent, and the time of the reaction. Compounds with a low boiling point, like dichloroethane, dichloromethane, chloroform, and carbon tetrachloride, have been used to study the esterification reaction. We found that the best solvent is dichloroethane. Dichloroethane, which was chosen as the best solvent, was used for all of the reactions.

When dichloroethane was utilized as the solvent, it was investigated how the molar ratio affected the yield. Salicylic acid and alcohol were mixed in various molar ratios. The molar ratio of salicylic acid to alcohol altered from 1:1 to 1:6. Figure 3 depicts the final result. The results demonstrate that the yield increases with the molar ratio of acid to alcohol up to molar ratios of acid to alcohol. Other requirements include 0.05 g of catalyst, dichloroethane as the solvent, 3 hours of time, and reflux.

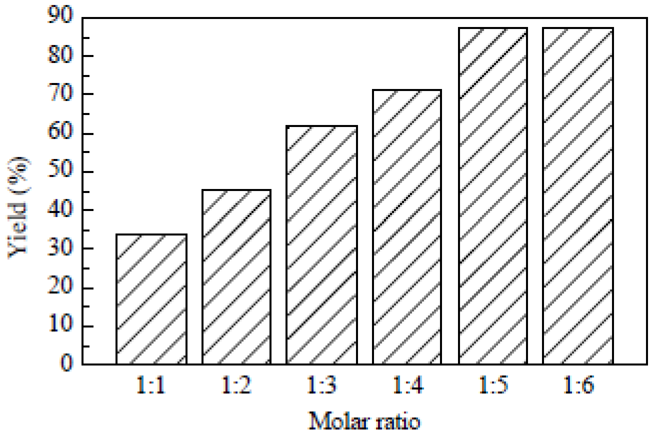


**Fig. 3.** "Esterification of salicylic acid with 1-pentanol with various"

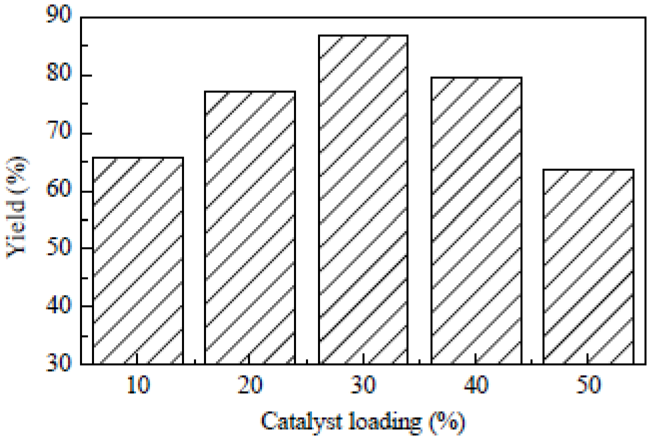


**Fig. 4.** "Esterification of salicylic acid with 1-pentanol with various loadings of catalyst. Other conditions: catalyst amount 0.05 g, molar ratio of acid:alcohol 1:5, solvent dichloroethane, time 3 h, reflux".

The acid is protonated on the catalyst's Bronsted acid site, following which alcohol is supplied and a water molecule is removed. The protonated acid reacts with the alcohol during the process, and if there is too much alcohol, the acid may not be able to reach the site of the reaction. As a result, the best ester yield was discovered when the acid-to-alcohol ratio was 1:5.

## CONCLUSION

The catalytic behavior of nanosized SiO2 with varying concentrations of Preyssler HPA in the esterification of salicylic acid with various aromatic and aliphatic alcohols has been investigated. When compared to other loadings, the catalyst with 30% wt showed the best catalytic activity and converted the most salycilic acid. When microwaves are utilized instead of traditional heating, esterification reactions occur faster. The amount of ester produced during the reaction was determined by the molar ratio of acid to alcohol, the temperature, the amount of catalyst used, and the duration of the reaction. The above catalyst could be recycled, saving money and being environmentally friendly. It could be employed in similar reactions as well. This research describes a new solid acid catalyst that can be used instead of liquid acids in critical organic chemistry reactions. This catalytic study may investigate the various applications of the Preyssler solid acid catalyst in business.

## REFERENCES

1. Kharissova, O. V., Kharisov, B. I., Oliva González, C. M., Méndez, Y. P., & López, I. (2019). Greener synthesis of chemical compounds and materials. *Royal Society open science*, *6*(11), 191378.
2. Jia, H., Du, D., Ma, K., Zhao, Y., Wang, Y., & Zhu, Z. (2017). Optimization and Process Intensification of Ketal Reaction in Industrial Ibuprofen Synthesis. *Chemical Engineering Transactions*, *61*, 691-696.
3. Ji, H. F. (2014). Past and Present Research Systems of Green Chemistry. *Green Chemistry*, *2014*.
4. Bamoharram, F. F., Heravi, M. M., Roshani, M., Jahangir, M., & Gharib, A. (2006). Preyssler catalyst,[NaP5W30O110] 14−: A green, efficient and reusable catalyst for esterification of salicylic acid with aliphatic and benzylic alcohols. Applied Catalysis A: General, 302(1), 42-47.
5. Heravi, M. M., Sadjadi, S., Sadjadi, S., Oskooie, H. A., Shoar, R. H., & Bamoharram, F. F. (2009). Silica-supported Preyssler nanoparticles as new catalysts in the synthesis of 4 (3 H)-quinazolinones. *South African Journal of Chemistry*, *62*(1), 1-4.
6. Gharib, A., Pesyan, N. N., Fard, L. V., & Roshani, M. (2014). Synthesis of Ibuprofen using silica-supported Preyssler nanoparticles ([H. sub. 14][Na [P. sub. 5][W. sub. 30][O. sub. 110]]/Si [O. sub. 2]) as an eco-friendly, inexpensive, and efficient catalyst. *Organic Chemistry International*.
7. Alimadadi, B., M Heravi, M., Nazari, N., Abdi Oskooie, H., & F Bamoharram, F. (2016). An efficient one-pot three-component synthesis of pyrido [2, 3-d] pyrimidine derivatives in the presence of nano silica-supported Preyssler H14

[NaP5W30O110]/SiO2 as a green and reusable catalyst. *Scientia Iranica*, *23*(6), 2717-2723.

8. Unterlass MM. 2016 Green synthesis of inorganic–organic hybrid materials: state of the art and future perspectives. Eur. J. Inorg. Chem. 2016, 1135–1156. (doi:10.1002/ejic. 201501130)
9. Alberto C, Ade M. 2013 Environmental sustainability: implications and limitations to Green Chemistry. Found. Chem. 16, 125–147. (doi:10.1007/s10698-013-9189-x).
10. Feng S, Li G. 2017 Hydrothermal and solvothermal syntheses. In Modern inorganic synthetic chemistry, pp. 73–104. Amsterdam, The Netherlands: Elsevier.
11. Ranu B, Stolle A. 2016 Ball milling towards Green synthesis: applications, projects, challenges. Johnson Matthey Technol. Rev. 60, 148–150. (doi:10.1595/205651316X691375).
12. Kitchen HJ et al. 2013 Modern microwave methods in solid-state inorganic materials chemistry: from fundamentals to manufacturing. Chem. Rev. 114, 1170–1206. (doi:10.1021/cr4002353)