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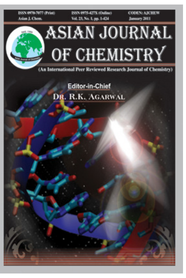

Nano-Preyssler Heteropolyacid: A Novel Nanocatalyst for Poly-Condensation of Benzyl Alcohols

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Silica-supported preyssler nanoparticles, behave as an effective nanocatalyst in poly-condensation of benzyl alcohol and its derivates. The polymer is characterized by ^{1}H NMR, IR and UV-vis spectroscopy.

Key Words: Nanocatalyst, Preyssler, Heteropolyacid, Polycondensation, Benzyl alcohol.

INTRODUCTION

Catalysts which are nanoparticles, composed of clusters of atoms, often metals, with particle size varying between 1-20 nm. There are two types of nanocluster catalysts that carry out chemical reactions with high rates and selectivity[1]. Enzymes are natural catalysts and many of them are composed of inorganic nanoclusters surrounded by high molecular weight proteins. These catalysts help the human body to function and are responsible for the growth of plants. They usually function at room temperature and in aqueous solution. Synthetic catalysts, either homogeneous or heterogeneous, are often metal nanoclusters that are used in the chemical technologies to carry out reactions with high turnover and selectivity. The heterogeneous systems have high catalyst surface area and they frequently operate at high temperatures. Because both enzymes and synthetic catalysts are usually nanoclusters in size, thus the fields of catalysis science and technologies are also nanoscience and nanotechnologies. Therefore the evolution of the fields of catalyst is strongly coupled to the development of nanoscience and nanotechnology.

In recent years, interest has focused on the synthesis and applications of nanocatalysts and along this line, polyoxometalates (POMs) are attracting much attention as building blocks for functional composite materials because of their interesting nanosized structures[2]. They are ideal models for the construction of hybrid systems, so they are regarded as the potential candidates to be transformed into nanometer-sized materials. Therefore, plenty of room exists for expanding the exploration of the opportunities for these materials and further exploring and development of new polyoxometalates is still a challenge for polyoxometalate chemistry.

As the particle size decreases, the relative number of surface atoms increases and not only the catalytic activity increases, but also it may show unique properties for several applications. It is expected that nanostructured polyoxometalates show higher catalytic activity than any of the other micron-sized particles. This point is very important in catalysis reactions. In addition, nano polyoxometalate compounds have several advantages as catalysts which make them economically and environmentally attractive.

Among a wide variety of polyoxometalate clusters have been reported to date[3], there are only three anions, $[NaSb_9W_{21}O_{86}]^-$, $[NaAs_4W_{40}O_{140}]^{25-}$ and $[NaP_5W_{30}O_{110}]^{14-}$ that have been reported to encapsulate rare-earth ions[4,5]. In the latter of these, $[NaP_5W_{30}O_{110}]^{14-}$, the so called preyssler anion, Na^+ is encrypted inside a central cavity formed by five PW_6O_{22} units arranged in a crown. This catalyst is green with respect to corrosiveness, safety, quantity of waste and separability. This catalyst is also unique, due to its stability in pH 0-12. However, not only the catalytic applicability of preyssler anion as bulk form, but also as nano structure form, has been largely overlooked.

Encouraged by our success in work with preyssler heteropolyacid as a green catalyst[6-14], it is great interest to know what occur if the preyssler anion is used as nanocatalyst. In continuation of our interest in the field of application of heteropolyacids we have developed our research in field of nanotechnology[15-23] and synthesized and characterized, silica-supported preyssler nanoparticles and studied its catalytic activity for photodegradation of methyl orange[16]. We also manipulate the synthesis and characterization of magnetite nanoparticles obtained by glycothermal method[17], synthesis of silver nanoparticles in the presence of $H_{14}[NaP_5W_{30}O_{110}]$ and their catalytic activity for photo degradation of methylene blue and methyl orange[15], synthesis of 4(3*H*)-quinazolinones with silica-supported preyssler nanoparticles[18], synthesis of isobenzofuran-1(3*H*)-ones with silica-supported preyssler nanoparticles[19], rapid and efficient synthesis of 4(3*H*)-quinazolinones under ultrasonic irradiation using silica-supported preyssler as nano form[20], synthesis of *bis*(indolyl)-alkanes under ultrasonic irradiation using silica-supported preyssler nanoparticles[21] and synthesis of 1,3-diaryl-5-spirohexahydropyrimidines[23]. In this work, we wish to report that preyssler nano catalyst is also active in polymerization reactions as well as above mentioned reactions. The main aim of the work described herein, is the design and development of applications for preyssler nanocatalyst in poly condensation of benzyl alcohols.

EXPERIMENTAL

Nanocatalyst preparation: Nano preyssler catalyst was obtained according to earlier work[16]. All of the chemicals were obtained from commercial sources. All yields were calculated from purified products.

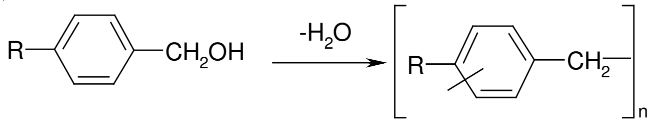
Poly condensation of benzyl alcohols

General procedure: The polycondensation reaction was carried out in a magnetically stirred glass reactor fitted with a reflux condenser and a thermometer. In a typical experiment, 6.2 mL of benzyl alcohol and 0.05 g nanocatalyst were refluxed. After few minutes, the mixture began to vigorous bubbling and in 2 min, the vigorous bubbling ceased and the system becoming highly viscous. On cooling, a resinous substance was obtained. The catalyst can be readily removed by shaking the chloroform solution with water and then filtration. The pure polymer in white color was isolated by dissolving solid in DMF and adding the solution to methanol. After three recrystalization, the obtained polymer was dried *in vacuum.*

RESULTS AND DISCUSSION

A preyssler catalyst consists of an anion with a formula of $[NaP_5W_{30}O_{110}]^{14-}$ which has an unusual 5-fold symmetry achieved by fusion of five $\{PW_6O_{22}\}$ groups. The central sodium ion lies not on the equator of the anion but in a plane roughly defined by oxygen atoms of the phosphate groups. The presence of the Na^+ reduces the overall anion symmetry from D_{5h} to C_{5v}[24]. In our previous work on silica-supported preyssler nano structures were synthesized through a micro emulsion method[16]. The sizes and morphology of products were controlled by changing the water to surfactant and reaction time. For a short time, the tubular structure prevailed, whereas the spherical shapes dominated at longer times. In this work, we have studied the role of synthesized preyssler nanoparticles for polycondenstion of benzyl alcohols. Effort to develop of a solid nanocatalyst for polymerization of benzyl alcohol and its derivatives has focused on the use of preyssler nanocatalyst for several reasons. This nanocatalyst has high inherent acidity, thermal and oxidative stability, high hydrolytic stability and is recyclable.

In addition, in spite of extensive investigations on Keggin nanocatalysts[25,26], the application of preyssler nanocatalyst has been largely overlooked. This catalyst promotes the polymerization of benzyl alcohols and shows excellent catalytic activity. The reaction is shown in **Scheme-I**.

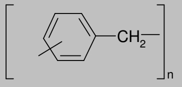
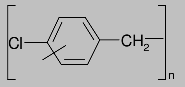
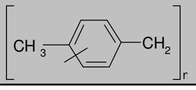


Scheme-I

The reactions were performed by refluxing of benzyl alcohol in presence of nano preyssler catalyst under solvent free conditions. The catalyst also heterogeneously catalyzed various derivatives of benzyl alcohols. Interestingly, the polycondenstion reaction over the silica-supported nano preyssler catalyst undergoes to completion with 100 % conversion of benzyl alcohols. The reaction time for obtaining the polybenzyls in 100 % yields was 3 min. The reaction in the presence of solvent such as toluene and benzene also gives the same polybenzyl as that obtained in a solvent free system, with a lower yield. Most probably in solvents benzyl alcohol undergoes side-reactions such as alkylation and condensation-etherization. The IR spectra of polybenzyls showed the disappearance of the original alcoholic -OH group.

^1H NMR intensities of benzene moieties, methyl substituent and benzyl methylene in the polymers indicate that the polycondensation takes place and the elimination of one -H of the benzene moiety of one reactant and one -OH group of another reactant confirms the conversion of benzyl alcohols. As a typical example, the NMR spectrum of the product of poly condensation of benzyl alcohol is shown in Table-1. Viscosities and melting points of polymers are given in Table-1 which indicate, the polymers have low molecular weight. The type of polymerization is most probably, a carbonium ion mechanism *via* the strong Bronsted acidity of nanocatalyst. It is suggested that an intermolecular condensation take places in *ortho* position *via*

TABLE-1
SPECTRAL AND EXPERIMENTAL DATA FOR OBTAINED POLYBENZYLS

Entry	Polybenzyl	^1H-NMR data	Viscosity	m.p. (°C)	Decomposition temp. (°C)
1		7.06 (phenyl), 3.86 (methylene)	0.190	48-83	530
2		7.08, 6.92 (phenyl), 3.98 (methylene)	0.058	88-120	465
3		6.80 (phenyl), 3.75 (methylene), 2.25,2.10 (methyl)	0.081	80-116	520

elimination of water. The dehydrogenation can take place and anthracene can from at the end of chain. The UV spectra supported this result *via* observation of same λ_{max} for anthracene and obtained polymers. At the end of the reaction, the catalyst could be recovered by a simple filtration. The recycled catalyst could be washed and subjected to a second run of the reaction process. The yields of reactions after using this catalyst for five times show only a slight reduction.

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