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Catalytic Performance of Nano-SiO_2-Supported Preyssler Heteropolyacid in Esterification of Salicylic Acid with Aliphatic and Benzylic Alcohols

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Abstract: An efficient and environmentally benign procedure for the catalytic esterification of salicylic acid with aliphatic alcohols, $C_nH_{2n+1}OH$ (n = 1–5) and benzylic alcohols, $RC_6H_4CH_2OH$ (R = H, NO_2, OCH_3, Br, Cl, Me) was developed using nano-SiO_2-supported Preyssler heteropolyacid both under thermal conditions and microwave irradiation. Silica nanostructures were obtained through a sol-gel method and were characterized by transmission electron microscopy and powder X-ray diffraction. The effects of various parameters such as solvent type, molar ratio of substrates, Preyssler heteropolyacid loading on silica, catalyst amount, temperature, and reaction time were studied and the optimum conditions were obtained. It has been found that the catalyst with 30 wt% loading is highly active and shows high yields in esterification reactions. The use of nano-SiO_2-supported Preyssler heteropolyacid coupled with microwave irradiation allows a solvent-free, rapid (3 min), and high-yielding reaction. This catalyst can be easily recovered and reused for many times without a significant loss in its activity.

Key words: Preyssler; heteropolyacid; silica; esterification; salicylic acid

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The esterification of salicylic acid with alcohols over acid catalysts is an important reaction in organic synthesis [1]. The increasing demand for safe industrial processes requires the development and implementation of environmentally friendly, solid catalysts for value-added, acid-catalyzed reactions.

Homogeneous acids such as H_2SO_4 and H_3PO_4 [2–4] represent the most commonly used catalysts for most of the important esterification reactions. However, these acids are corrosive, hazardous, used in more than stoichiometric amounts, and difficult to recover from reaction mixtures. They also cannot be reused and lead to low selectivity for desired products and produce a large volume of environmentally hazardous acidic waste. New environmental rules call for the reduction of waste production and use of more environmentally friendly alternative catalysts. The substitution of traditional homogenous Lewis and Brönsted acid catalysts by heterogeneous ones, e.g. solid acid catalysts such as sulfated zirconia, zeolites, and acidified silica [5] constitutes a more environmentally friendly alternative to the organic reactions [6].

As known, solid heteropolyacids (HPAs) and their derivatives have been intensively studied because they can be used as excellent acidic, redox, and bifunctional catalysts in catalytic reactions [7–9]. In this area, increasing attention has been paid to search for preparing supported HPA catalysts. Efforts have also been made to study the support of HPAs on suitable nano supports [10,11]. The use of supported HPAs increases the specific surface area of the catalysts and modifies their catalytic properties. Catalytic properties can increase using nano supports. Thus, immobilization of HPAs on a number of supports was extensively studied. Silica, alumina, and active carbon were the most investigated supports [12–16]. It has been found that HPAs supported on SiO_2 are most stable. It is due to their high thermal stability, unique pore system, and numerous possibilities to modify their composition, morphology, and sorption properties.

The objective of this paper is to enhance the catalytic properties of Preyssler catalyst, with formula of $H_{14}[NaP_5W_{30}O_{110}]$, via supporting it on nano-SiO_2 for esterification of salicylic acid with aliphatic and benzylic alcohols.

The structure of the anion $[NaP_5W_{30}O_{110}]^{14-}$ is formed by a cyclic assembly of five $\{PW_6O_{22}\}$ groups. The unusual 5-fold symmetry of this anion is 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 [17]. Our research group has developed catalysis with Preyssler HPA for a broad range of organic syntheses and environmentally benign catalysis during the past few years [18–27]. Good yields, high selectivity, economical convenience, ease of work up, high hydrolytic and thermal stability, and high catalytic activity of Preyssler HPA [28–34] have indicated high potential for nano-catalysis in organic synthesis and environmentally benign catalysis.

To the best of our knowledge there is no literature report on the use of nano-silica supported Preyssler HPA as catalyst in esterification of salicylic acid. Recently, we systematically investigated the catalytic behavior of Preyssler HPA for many acid-catalyzed reactions and found that this catalyst is more active than the other catalysts [35–40]. In order to perform a new contribution to the field of eco-friendly, acid-catalyzed reactions coupled with nanotechnology, we report here on the results of esterification of salicylic acid with aromatic and aliphatic alcohols using Preyssler HPA supported on nano-silica under thermal and microwave conditions.

1 Experimental

1.1 Synthesis of SiO_2 nanoparticles

The material used in this work as the SiO_2 precursor is tetraethyl orthosilicate (TEOS, Merck, 98%). Besides the main precursor, nitric acid (Arman Sina, 65%) and double distilled water were used for peptization and as solvent, respectively. The sol-gel precursor solution was obtained by mixing of TEOS and ethanol with EtOH/TEOS molar ratio of 4. The mixture was stirred using magnetic stirring. At a pH value of 2 forms a clear solution. The molar ratio of water to TEOS was 12. After the specified solution was obtained for 20 min, it was poured in a clean container and left at ambient temperature for gelation. After the gel had formed, the gelation time was calculated for the sample. The final step in the process consisted of drying the sample at 220 °C for 6 h. The gelation time is defined as the time between pouring the solution in the container and the time at which the solution ceases to discernibly flow under the influence of gravity.

1.2 Catalyst preparation

$H_{14}[NaP_5W_{30}O_{110}]$ was prepared according to our earlier work [18]. For the preparation of supported catalyst, the synthesized nano-silica was suspended in 20 ml of water and then the heteropolyacid with different loadings of tungsten was added to this suspension. After stirring the heterogeneous solution-support mixture, the solvent was evaporated, samples were dried at 120 °C and the catalysts were calcined at 250 °C in a furnace prior to use.

1.3 Catalyst characterization

Infrared (IR) spectra were recorded on a Buck scientific 500 spectrometer (KBr pellets). The particle size and shape of nanostructures of SiO_2 were studied by transmission electron microscopy (TEM, LEO 912 AB). The X-ray diffraction (XRD) patterns of the samples were obtained using a PW3710-Philips powder diffractometer (Cu K_α irradiation). BET specific surface areas, pore sizes, and pore volumes were calculated from nitrogen adsorption isotherms using an Autosorb-1 Quantachrome instrument.

1.4 Catalytic test

In a typical reaction, 1-pentanol, salicylic acid, and nanocatalyst were put in a glass reactor and the reaction mixture was stirred and refluxed at the boiling point of solvents for 3 h. At room temperature (25 °C) reactions were carried out with stirring for 6 h. At regular intervals, Karl-Fischer- titration was performed for determination of the produced water. The products were characterized by comparison of their spectroscopic data with those of authentic samples. Yields were determined by gas chromatography (Pu 4500 gas chromatograph with an FID detector; HP-5 column, 30 m × 0.32 mm i.d. × 0.25 μm film thickness). The GC process started at 70 ºC and the temperature was raised with a rate of 15 ºC/min. Under microwave irradiation a solution of salicylic acid, alcohol, and nanocatalyst was irradiated for 3 min. A MILESTONE APC-55E microwave (450 W, 80 °C) was used in all of the experiments.

2 Results and discussion

2.1 Characterization results

In our previous work, we investigated performance and capability of sodium-30-tungstopentaphosphate, the so-called Preyssler's anion, for highly selective and efficient esterification of salicylic acid with some aliphatic and ben-

zylic alcohols [18] in the presence of different forms of Preyssler catalyst, i.e. in pure form, as mixed addendum, and silica-supported. The results of the comparison between supported and non-supported Preyssler HPA have shown that in all cases the supported polyacid is less active than the non-supported one. Therefore, it is of great interest to know what occurs if the nano-SiO_2-supported Preyssler HPA is used in this esterification reaction. Interestingly, we have found that the nano-SiO_2-supported Preyssler catalyst renders the esterification reaction more effective in an organic solvent than SiO_2-supported Preyssler catalyst.

Silica nanostructures were obtained through a sol-gel method. All of the conditions are shown in the experimental section. The BET surface area, pore volume, and average pore size of nanosized SiO_2 were obtained as 287 m^2/g, 0.28 cm^3/g, and 0.25 nm, respectively. After the impregnation of HPA (with 30% being the best loading), the BET surface area, pore volume, and average pore size were obtained as 201 m^2/g, 0.10 cm^3/g, and 0.21 nm, respectively. The BET surface area and pore volume decreased, indicating that the pores of nanosized silica are being filled and the supported HPA blocked some pores of the support.

The obtained nano structures were characterized by TEM as shown in Fig. 1. This figure shows 40 nm spheres. The XRD pattern of nano-SiO_2 with sharp peaks in the 2θ range from 7º to 36º confirmed the crystalline nature of SiO_2. In addition, lack of an XRD peak centered at 2θ angle 22º (typical for amorphous SiO_2) confirmed the crystallinity. The patterns of the spherical products confirm the SiO_2 structure.

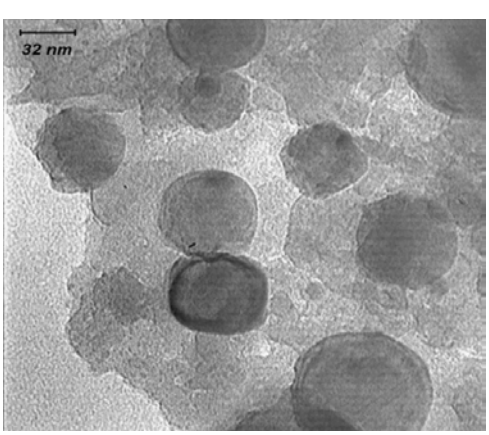

Fig. 1. TEM image of the synthesized nano-SiO_2.

The heteropolyacid $H_{14}[NaP_5W_{30}O_{110}]$ in the SiO_2 nano particles was confirmed by IR spectroscopy as shown in Fig. 2. The asymmetric stretching frequency of the terminal oxygen is observed at 960 cm^{-1} and the P–O asymmetric stretching frequency is noted at 1080 and 1165 cm^{-1}. The prominent P–O bands at 960, 1080, and 1165 cm^{-1} are consistent with a C_{5v} symmetry anion. These bands demonstrate

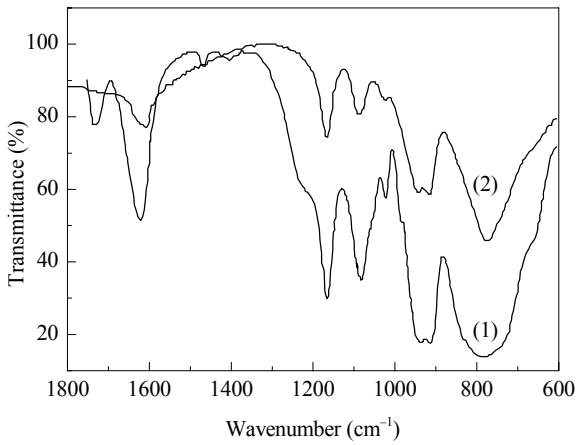

Fig. 2. IR spectra of Preyssler heteropolyacid in bulk form (1) and nano form (2).

that $H_{14}[NaP_5W_{30}O_{110}]$ is preserved in the HPA/SiO_2 nano particles. In addition, the protonated water band of $H_{14}[NaP_5W_{30}O_{110}]$ also remained noticeable in the nanoparticles at 1730 cm^{-1}. It could be confirmed that the heteropolyacid $H_{14}[NaP_5W_{30}O_{110}]$ was successfully immobilized within the SiO_2 nanoparticles since the heteropolyacid does not react with SiO_2 or with water, but it can remain in the silica nanoparticles without appreciable change of the structure.

2.2 Catalytic activity

In order to evaluate the catalytic activity of nano-SiO_2-supported Preyssler catalyst for the esterification of salicylic acid, the reaction was optimized for the esterification with 1-pentanol. The effects of various parameters such as solvent type, amount of the catalyst, temperature, loading percentage, and time of reaction were studied. The esterification reaction in various solvents with low boiling points, such as dichloroethane, dichloromethane, chloroform, and carbon tetrachloride has been explored. We have found that dichloroethane is the best solvent. All of the reactions were carried out in dichloroethane as the solvent of choice.

The influence of molar ratio on yield in dichloroethane as solvent was investigated. Various molar ratios of salicylic acid to alcohol were used. The molar ratio of salicylic acid:alcohol was varied as 1:1 to 1:6. The results are shown in Fig. 3. The results show that the yield increases with the molar ratio up to 1:5. The mechanism involves protonation of the acid on the Brönsted acid site of the catalyst followed by addition of alcohol and elimination of a water molecule. During the reaction, the protonated acid interacts with alcohol and a too large alcohol fraction may hinder access of the acid to the catalytic site. In view of this, the optimum ester yield was obtained with acid:alcohol molar ratio of

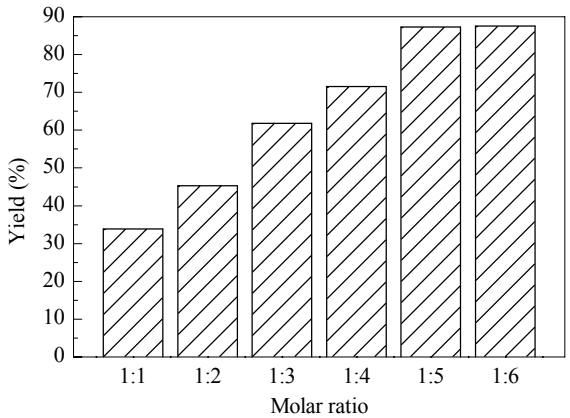

Fig. 3. Esterification of salicylic acid with 1-pentanol with various molar ratios of acid:alcohol. Other conditions: catalyst amount 0.05 g, solvent dichloroethane, time 3 h, reflux.

1:5.

In order to examine the effect of Preyssler anion loading on silica, catalysts with different initial Preyssler HPA loadings (10%–50%) on nano-silica were prepared. The results are shown in Fig. 4. The results show that the highest yield can be achieved with 30% loading. The yield increases with an increase in Preyssler HPA loading on silica from 10% to 30%. It is attributed to the increase in the total number of available active catalytic sites for the reaction. Higher Preyssler anion loadings on silica (> 30%) affected yields and gave lower yield of esters, which can be likely attributed to side reactions catalyzed by the excess amount of acidic sites. The fall of the yield at high catalyst loading was also attributed to competitive adsorption between the additives and the substrates at the active sites on the catalyst surface or physically blocking of the catalyst pores by excessive amounts of additives. Thus 30% loading is the optimum condition for the esterification reaction.

After optimizing the percentage loading, we endeavored

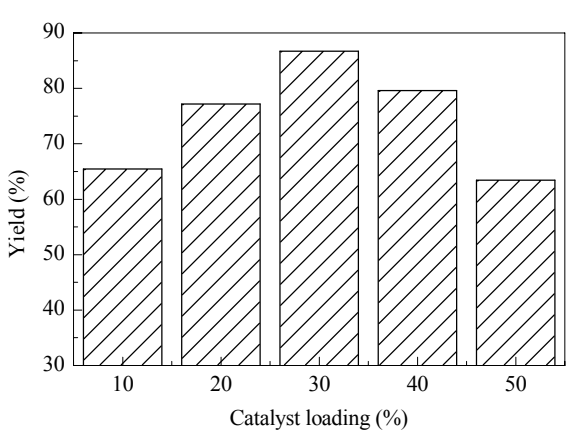

Fig. 4. Esterification of salicylic acid with 1-pentanol with various loadings of catalyst. Other conditions: catalyst amount 0.05 g, molar ratio of acid:alcohol 1:5, solvent dichloroethane, time 3 h, reflux.

Table 1 Yields of esterification of salicylic acid with 1-pentanol using various amounts of the nanocatalyst

Catalyst amount (g)	Yield (%)
0.01	49
0.02	67
0.03	73
0.04	80
0.05	89
0.06	89

Reaction conditions: molar ratio of acid:alcohol 1:5, solvent dichloroethane, time 3 h, reflux.

to optimize the amount of the catalyst. The observations are presented in Table 1. The esterification reaction was conducted by varying the catalyst amount from 0.01 to 0.06 g by keeping all of the other parameters constant. The results in Table 1 indicate that the yield increases with the catalyst amount up to 0.05 g. Any further increasing does not have any appreciable effect on the reaction yield. It is suggested that the ester yield reaches a steady value with increase in catalyst amount, which can be attributed to reaching the equilibrium value of the ester yield.

The effect of reaction time on the esterification reaction of salicylic acid was also studied (Fig. 5). The results indicate that there is an increase in the amount of product with increase of reaction time. The optimum reaction time has been found to be 3 h at reflux temperature and any further increase did not have any appreciable effect on the reaction yield. It is important to note that the esterification reaction is an equilibrium reaction and due to this, the ester yield increases with time till it reaches the equilibrium value, and there is no further increase beyond equilibrium value with further raise of reaction time.

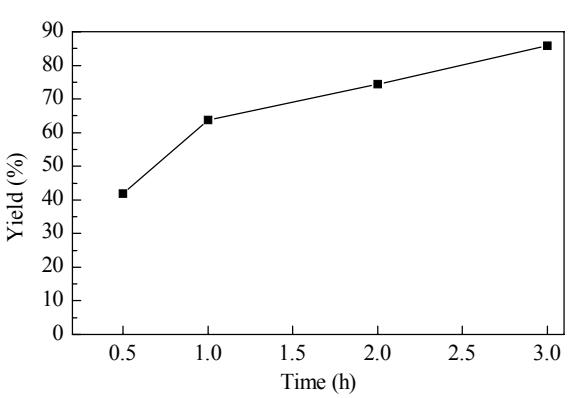

Fig. 5. Esterification of salicylic acid with 1-pentanol at different times. Other conditions: catalyst amount 0.05 g, molar ratio of acid:alcohol 1:5, solvent dichloroethane, reflux.

The esterification reactions were carried out at two temperatures including room temperature (RT, lowest temperature) and reflux temperature (highest temperature). The

maximum yield of ester is reached at the reflux temperature. This was expected since increasing the temperature is apparently favorable for the acceleration of the forward reaction. In general, the yields are lower when the reactions are carried out at room temperature. Also this can be attributed to the fact that the esterification is an endothermic reaction. Hence the reaction product yield increases with temperature enhancement.

After optimizing the conditions, we examined the generality of these conditions to other alcohols with different initial Preyssler catalyst loadings (10%–50%) on nano-silica. Under these conditions, a series of experiments were tested (Table 2). Interestingly, in all cases the observed yields were highest with 30% loading.

Table 2 Yields of esterification of salicylic acid with aliphatic and benzylic alcohols under room temperature and reflux conditions

Alcohol	Yield of ester (%)									
	10% catalyst loading		20% catalyst loading		30% catalyst loading		40% catalyst loading		50% catalyst loading	
	RT	Reflux	RT	Reflux	RT	Reflux	RT	Reflux	RT	Reflux
Methanol	45	60	48	72	53	82	46	74	41	58
Ethanol	46	62	49	74	56	85	49	78	44	62
1-Propanol	48	74	51	76	58	86	50	79	45	64
2-Propanol	26	30	30	43	36	53	33	46	28	30
Butanol	46	66	50	78	57	87	52	70	48	55
t-Butanol	24	25	27	39	31	44	28	42	24	26
1-Pentanol	48	68	52	80	59	89	54	85	50	79
2-Pentanol	43	45	47	56	43	67	28	60	25	45
Benzyl alcohol	28	44	31	54	35	63	30	56	27	36
4-Metoxy benzyl alcohol	29	55	42	67	49	77	42	70	37	55
2-Methyl benzyl alcohol	35	57	38	64	44	73	38	65	34	40
2-Chloro benzyl alcohol	32	50	35	60	39	59	33	52	29	39
4-Bromo benzyl alcohol	26	34	29	43	34	53	28	47	24	32
3-Nitro benzyl alcohol	25	32	28	40	32	49	27	42	23	30

Reaction conditions: catalyst amount 0.05 g, molar ratio of acid:alcohol 1:5, solvent dichloroethane, time 3 h (for reflux condition) or 6 h (for room temperature).

2.3 Microwave irradiation

Esterification under microwave irradiation, besides being environmentally friendly, is also marked by a considerable reduction of reaction time in comparison to conventional esterification [41,42]. Furthermore, to the best of our knowledge, esterification of salicylic acid with silica-supported nano-Preyssler catalyst has not yet been achieved under microwave irradiation. To determine the potential of this new catalytic system, the esterification reactions were carried out under the optimized conditions under microwave irradiation. The results are shown in Table 3. As we can see, this catalyst afforded excellent yields in very short time (3 min). Since we had high yields of products and recyclable catalysts, we can tell that the reactants should absorb microwave irradiation for conversion while the catalyst and products were stable.

A dramatic change in the way of chemical synthesis can be achieved by microwave irradiation. The efficiency of the microwave-based process lies not only in the reduction of reaction time from hours to minutes, but it is also known to reduce side reactions, enhance yields, and improve reproducibility. Besides the efficient energy input that microwaves can provide to the reaction mixtures, a chemical activation effect cannot be discounted. During the irradiation, there is a total or partial alignment of dipolar molecules and/or ionic species with the direction of the electrical field. Such an alignment may then favor interactions between reactants and may lead to shorter and more efficient reactions.

2.4 Reusability of the catalyst

In order to further evaluate the performance of the catalyst, reuse experiments of the catalyst were carried out. The catalyst was filtered at the end of the reaction. The obtained precipitate was washed with water and dried. The catalyst was reused for the next run under the same conditions. The results indicated that the activity of the catalyst was not affected even at the third run with the reused catalyst. This phenomenon implied that the catalyst can be efficiently recovered and recycled without any significant loss of activity, as the catalyst remained active even after the third cycle (86% yield). Thus there is not leaching. By this token, the catalyst possesses application potential in industry.

Table 3 Yields of esterification in the presence of nano-SiO_2-supported Preyssler HPA under microwave irradiation

Alcohol	Yield of ester (%)				
	10% catalyst loading	20% catalyst loading	30% catalyst loading	40% catalyst loading	50% catalyst loading
Methanol	70	80	89	81	72
Ethanol	74	83	91	84	76
1-Propanol	77	85	92	85	79
2-Propanol	56	61	98	63	58
Butanol	77	84	92	85	79
t-Butanol	51	57	63	58	53
1-Pentanol	87	96	89	81	79
2-Pentanol	70	77	72	66	64
Benzyl alcohol	57	64	74	66	59
4-Metoxy benzyl alcohol	71	78	85	80	73
2-Methyl benzyl alcohol	68	75	82	77	70
2-Chloro benzyl alcohol	63	69	75	71	66
4-Bromo benzyl alcohol	57	62	68	64	60
3-Nitro benzyl alcohol	55	60	66	62	57

Reaction conditions: catalyst amount 0.05 g, molar ratio of acid:alcohol 1:5, solvent dichloroethane, time 3 min, power 450 W, temperature 80 ºC.

3 Conclusions

Nano-sized SiO_2 with different loading of Preyssler HPA has been synthesized and the catalytic behavior of it has been studied in the esterification of salicylic acid with different aromatic and aliphatic alcohols. The catalyst with 30 wt% loading showed good catalytic activity with a maximum conversion of salycilic acid as compared with other loadings. Esterification reactions were found to occur faster with microwave irradiation than with conventional heating. The molar ratio of acid to alcohol, temperature, catalyst amount, and reaction period influenced the ester yield during the reaction. The above catalyst was recyclable, cost effective, and environment friendly and could be used in similar reactions. This research reports a new solid acid catalyst for the replacement of traditional liquid acids in important reactions and introduces a new catalyst for organic chemistry. This catalytic study may explore the wide application of Preyssler solid acid catalyst in industry.

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