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SHORT COMMUNICATION

ACETYLATION AND OXYGENATION TRANSFORMATIONS CATALYZED BY SILICA-SUPPORTED DODECATUNGSTOPHOSPHORIC ACID

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ABSTRACT. Acetylation of alcohols in refluxing ethyl acetate, and oxidation of aniline and cyclohexanol with 34 % H_2O_2 in the presence of $H_3PW_{12}O_{40}$ and its supported forms on SiO_2 (20 %, 40 %, and 60 % by weight) as active solid acid catalysts were performed under mild reaction conditions with moderate to good yields and with 100 % selectivity. It is found that the supported $H_3PW_{12}O_{40}$ was in general 1.4-2.3 times more efficient than the unsupported catalyst in the acetylation and oxygenation reactions. Easy work-up and effective recycling of the heterogeneous catalyst were distinct advantages of the catalytic heterogeneous system.

KEY WORDS: Acetylation, Oxygenation, Dodecatungstophosphoric acid, Heterogeneous, Silica support

INTRODUCTION

The acetylation of alcohols is an important transformation in organic synthesis. It provides an efficient and inexpensive method for the protection of the hydroxyl group in a multi-step synthetic process [1]. There are several procedures for the acetylation of alcohols using acid anhydrides and acyl chlorides in the presence of trialkyl amines such as triethylamine and pyridine [2-4]. However, there is still a great demand for acid catalysts to generate esters under mild conditions and in processes that are environmentally benign.

Selective oxidation of alcohols and aromatic amines with aqueous hydrogen peroxide under mild conditions has attracted both considerable intellectual interest and potential utility. To date a variety of oxidation methods (stoichiometric and catalytic) have been reported for these reactions and many use soluble salts of transition metal cations [5-9]. The product composition in these reactions depends on the oxidant, catalyst, and reaction condition employed [10].

Catalysis by heteropoly acids (HPAs) and related polyoxometalates is a field of increasing importance [11]. HPAs have several advantages as catalysts which make them both economically and environmentally attractive, viz strong Bronsted acidity, exhibiting fast reversible multi-electron redox transformations under rather mild conditions, very high solubility in polar solvents, fairly high thermal stability in the solid state, and efficient oxidizing ability.

It has been recently found that Keggin-type heteropoly acids and acidic heteropoly salts are important catalysts for several homogeneous and heterogeneous catalytic transformations [12-17]. Though, there are many advantages, the main disadvantages of HPAs as catalysts lie in their low thermal stability, low surface area (1-10 m^2/g) and separation from reaction mixture. Thus, the development of new solid catalyst with advanced characteristics of strength, surface area, porosity, etc. has been a challenge for a long time. The supporting of HPAs on the suitable support is expected to overcome the mentioned problems of HPAs.

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Esterification and oxidation reactions in the presence of Keggin and Dawson tungsten HPAs as homogeneous catalysts have been extensively studied [11, 14-17]. Generally, such reactions are performed in organic media, and water greatly affects the reaction rate [17, 18]. Furthermore, since HPAs are soluble only in wet nucleophilic solvents, their intrinsic strong acidity cannot be fully utilized in homogeneous systems. In heterogeneous conditions, as well as in homogeneous systems, HPAs are generally more efficient than conventional catalysts, such as SiO_2-Al_2O_3, zeolites, etc., which is in line with their relative acid strengths [17, 19-20]. An obvious advantage of heterogeneous systems over homogeneous ones is easy separation of the catalyst from the reaction products.

Herein we report a new, efficient, and environmentally benign heterogeneous catalysis by the strongest heteropoly acid, $H_3PW_{12}O_{40}$ (PW) and its supported forms on SiO_2 (20 %, 40 %, and 60 % by weight) to the acetylation of some primary, secondary, and tertiary alcohols in refluxing ethyl acetate. Furthermore, selective and fast oxidation of aniline to nitrosobenzene and cyclohexanol to cyclohexanone with hydrogen peroxide are also discussed.

EXPERIMENTAL

General

All the products were characterized by a comparison of their spectral and physical data with those of known samples. The purity of the substances and the progress of the reactions were monitored by TLC on silica gel or by gas chromatography. GLC analyses were performed on a Shimadzu 17A-GC with a flame ionization detector using a 25 m x 0.25 mm capillary column packed with CPB_{10} as stationary phase. n-Decane was used as internal standard for GLC analyses. The heteropolyoxometalate $H_3PW_{12}O_{40}$ was prepared according to the literature method [24] or was purchased commercially. Silica-supported $H_3PW_{12}O_{40}$ catalysts were prepared by impregnating Aerosil 300 silica (SBET = 300 m^2g^{-1}) in a methanolic solution of $H_3PW_{12}O_{40}$ [25].

General procedure for acetylation of alcohols in the heterogeneous system

The catalyst (0.003 mmol, based on $H_3PW_{12}O_{40}$) was added to a mixture of ethyl acetate (4 mL) and alcohol (2 mmol) and the reaction mixture was stirred at 75 °C for the length of time indicated in Table 1. Progress of the reaction was followed by the aliquots withdrawn directly from the reaction mixture, analyzed by gas chromatography using internal standard or by TLC using ethyl acetate and hexane (1/5) mixture. After completion of the reaction, the reaction mixture was filtered off. Then, the supported catalyst was washed with dichloroethane at room temperature, followed by vacuum drying at 150 ºC for 1.5 h. The recycled catalyst can be reused several times for the acetylation reactions without any significant loss of catalytic activity. The filtrate was dried under vacuum to evaporate ethyl acetate and dichloroethane. Then, ether was added. Evaporation of the organic solution was followed by column chromatography on a short pad of silica gel using petroleum ether as eluent to afford the corresponding alkyl acetate as a liquid.

General procedure for oxidation of aniline and cyclohexanol

To a stirred solution of catalyst (0.003 mmol for aniline and 0.006 mmol for cyclohexanol, based on $H_3PW_{12}O_{40}$), and 34 % H_2O_2 (8 mmol for aniline and 1.5 mmol for cyclohexanol) in $CHCl_3$ (7 mL for aniline and 2 mL for cyclohexanol) was added substrate (4.4 mmol for aniline oxidation and 1.4 mmol for cyclohexanol oxygenation). The reaction mixture was stirred at room temperature (for the oxidation of aniline) and at 70 ºC (for the oxygenation of cyclohexanol) under air for the required times. Progress of the reaction was followed by GLC analysis of the aliquots withdrawn directly and periodically from the reaction mixture. At the end of the reaction, the unreacted hydrogen peroxide was decomposed and the organic solvent was evaporated. Then, the remaining products were extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate, filtered, and was concentrated under reduced pressure. In the case of aniline oxidation, the extract was purified by column chromatography on silica gel (2/5, ethyl acetate/hexane); whereas, for cyclohexanol oxygenation the concentrated above solution (extract) was treated with 2,4-dinitrophenylhydrazine in 6 % HCl to give 2,4-dinitrophenylhydrazone of cyclohexanone. The boiling point and spectral data of each product were compared with those of authentic samples and literature values.

The solid acid catalyst in the heterogeneous system was recycled as described in the previous section. Thereafter, the recycled catalyst could be reused for several times. However, the catalyst activity was gradually declining in successive runs.

RESULTS AND DISCUSSION

Table 1, shows the results of the acetylation of some alcohols in refluxing ethyl acetate catalyzed by $H_3PW_{12}O_{40}$ and its supported forms on SiO_2. The tertiary alcohol, *t*-butanol, exhibited with the highest activity among the examined alcohols, giving 60-90 % yield, whereas cyclohexanol displayed the least activity, resulted in only 10-23 % of cyclohexyl acetate in homogeneous and heterogeneous systems. 1-Butanol and benzyl alcohol showed modest activity and led to 36-83 % of 1-butyl acetate and 30-53 % of benzyl acetate, respectively, with the examined catalysts under the same reaction conditions.

It is noted that the heterogeneous system was clearly more effective than the homogeneous system in the acetylation of 1-butanol. Only 36 % of 1-butyl acetate was obtained in the homogeneous system after 3.5 h, whereas 83 % conversion was obtained with 20 % (PW)/SiO_2 after the same time and under similar reaction conditions. 20 % (PW)/SiO_2 was nearly 1.4-1.6 times more active than $H_3PW_{12}O_{40}$ in the acetylation of *t*-butanol, benzyl alcohol, and cyclohexanol. The other two supported catalysts, 40 % (PW)/SiO_2 and 60 % (PW)/SiO_2, were also more reactive than the unsupported catalyst in the acetylation reactions. Therefore, it appears that 60 % (PW)/SiO_2 was more effective than 40 % (PW)/SiO_2 in the acetylation of alcohols.

Table 1. Comparison of reactivity of $H_3PW_{12}O_{40}$ with the supported catalysts (PW/SiO_2) in the acetylation of some alcohols*.

Catalyst	1-Butanol		*t*-Butanol		Benzyl alcohol		Cyclohexanol	
	Yield %	Time (h)	Yield %	Time (h)	Yield %	Time (h)	Yield %	Time (h)
$H_3PW_{12}O_{40}$	36	3.5	60	3	30	2.5	10	7
20 % PW/SiO_2	83	3.5	85	3	45	2.5	16	7
40 % PW/SiO_2	77	3.5	90	3	50	2.5	18	7
60 % PW/SiO_2	82	3.5	90	3	53	2.5	23	7

*Alcohol (2 mmol) was added to a solution of heteropolyacid (0.003 mmol) in ethyl acetate (4 mL, 40 mmol) and the reaction mixture was allowed to stir at 75 °C for the required time. Mole ratio of catalyst:alcohol:ethyl acetate was 1:666:13332. Progress of the reaction was followed by withdrawing aliquots directly from the reaction mixture for GLC or TLC analyses. Isolated yields were based on the starting materials. All products were characterized by a comparison of their spectral and physical data with those of known samples.

Oxidation of aryl amines is an important reaction in the synthesis of oxygenated derivatives such as hydroxylamine, nitroso, nitro, oxime, azo and azoxy compounds. Azobenzene has been utilized as dyes, analytical reagents, reducing agents, stabilizers, liquid crystals and polymerization inhibitors and exhibits several physiological activities [21-23]. Therefore, a simple synthetic route for selective oxidation of aromatic amines to azobenzene is well documented.

Table 2 describes the oxidation of aniline into nitrosobenzene with 34 % H_2O_2 with complete selectivity catalyzed by homogeneous and heterogeneous systems under air at room temperature in chloroform. Nitrosobenzene monomer, as the major product, was formed as a clear green-colored solution, which was converted into its dimeric form as yellowish solid after evaporation of chloroform. According to the results, the heterogeneous system was nearly 1.6-2.2 more efficient than the homogeneous system in the oxidation of aniline. It is found that 60 % PW/SiO_2 was more effective than 40 % PW/SiO_2, and the later was more reactive than 20 % PW/SiO_2 in the oxidation of aniline. They produced 63, 54 and 45 % of nitrosobenzene, respectively, compared to 28 % yield obtained using homogeneous $H_3PW_{12}O_{40}$ catalyst, after 2 h.

We also examined the reactivity of the homogeneous and heterogeneous oxidation systems in the oxygenation of cyclohexanol. The results in Table 2 show that the homogeneous system was 1.6-2.3 less effective than the heterogeneous one. As in the oxidation of aniline, 60 % PW/SiO_2 was the most effective heterogeneous catalytic system, and 20 % PW/SiO_2 was the least reactive heterogeneous catalytic system. 20 % PW/SiO_2, 40 % PW/SiO_2, and 60 % PW/SiO_2 resulted in 37 %, 46 %, and 54 % of cyclohexanone, respectively, with 100 % selectivity under the above reaction conditions after 2.5 h.

Table 2. Homogeneous and heterogeneous oxygenation of aniline and cyclohexanol with H_2O_2 catalyzed by $H_3PW_{12}O_{40}$.

Substrate	$H_3PW_{12}O_{40}$ Yield %	20 % PW/SiO_2 Yield %	40 % PW/SiO_2 Yield %	60 % PW/SiO_2 Yield %	60 % PW/SiO_2 Yield %	Time (min)
Aniline[a]	28	45	54	63	63	120
Cyclohexanol[b]	23	37	46	54	54	150

[a] Aniline (4.4 mmol) was allowed to react with 34 % H_2O_2 (8 mmol) in the presence of catalyst (0.003 mmol) in $CHCl_3$ (7 mL) under air at room temperature for 120 min. The corresponding product, nitrosobenzene, was produced with >95 % selectivity. The minor product was nitrobenzene.

[b] Cyclohexanol (1.4 mmol) was allowed to react with 34 % H_2O_2 (1.5 mmol) in the presence of catalyst (0.006 mmol) in $CHCl_3$ (2 mL) under air at 70 °C for 2.5 h. Cyclohexanone was formed with 100 % selectivity.

The relative reactivity of $H_3PW_{12}O_{40}$ and its supported forms was dependent primarily upon their acidic strengths [15]. Other properties such as oxidation potential of the metal center, which determines the reducibility of HPA by the reaction medium, as well as the thermal and hydrolytic stability were also important. It is found that tungsten HPAs were the catalysts of choice for acetylation and oxidation reactions because of their stronger acidity, higher thermal stability, and lower oxidation potential compared to molybdenum HPAs. Moreover, the supported HPA catalysts were easily separated from the heterogeneous system by simple filtration and were reused without any considerable reduction in their catalytic activity.

In conclusion, an eco-friendly, clean, and cheap heterogeneous catalytic acetylation and oxygenation protocol is described under mild reaction conditions using $H_3PW_{12}O_{40}$ as the simplest heteropoly acid supported on SiO_2. Simple procedure, easy work-up, and using regenerable catalyst were of other advantages of this method.

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