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Liquid phase bromination of phenols over silicotungstic acid immobilized on nickel oxide nanoparticles

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Abstract

In this work, Liquid phase bromination of phenols was performed with silicotungstic acid immobilized on nickel oxide nanoparticles as heterogeneous catalyst. This catalyst was prepared by sol-gel method using heteropoly acids. The obtained composite was characterized by XRD, FT-IR and ICP technique. In this work, we have reported bromination of phenol, its derivatives and some aromatic compounds. The liquid phase bromination of phenol was performed using heteropoly acids immobilized nanoparticle of nickel oxide as catalyst, KBr as brominating agent and hydrogen peroxide as an oxidant in acetonitrile at room temperature. The reaction proceeds through the formation of Br^+ (bromonium ion), which attacks the phenol ring forming different brominated products. Prepared catalyst can be used several times without a significant decline in catalytic activity.

Keywords: Silicotungstic acid; bromination; phenol; sol-gel.

Introduction

Introduction of bromine into organic molecules is an important and fundamental reaction in many industrial processes; in a view of their importance in organic synthesis, brominated aromatic compounds are important as pharmaceuticals, agrochemicals, manufacture of dyes, flame-retardants and specialty chemicals [1,2]. A variety of methods for the electrophilic bromination of aromatic have been reported in the literatures [3,4]. Brominated aromatic compounds are widely used as building blocks for pharmaceuticals, and other specialty chemicals. Most of the aromatic compounds are poorly soluble in water, and this has been a major limitation in the preparation of industrially-important brominated compounds under aqueous conditions. Classical nuclear bromination of aromatic compounds involves the use of: (a) Bromine; (b) A catalyst like FeCl3, FeBr3, iodine, thallium acetate etc; (c) Absence of light, often yielding undesired Co-products. Bromination using HBr as a bromine source, H_2O_2 as an oxidant which was thought to be possible solution to overcome the aforementioned difficulties met with partial success, since HBr is highly toxic and corrosive as harmful as molecular bromine to the environment [5]. Mechanistically, it is believed that

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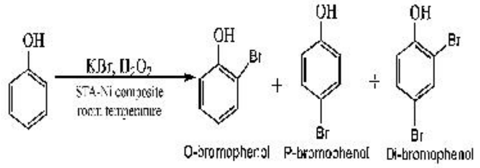
bromination of aromatics proceeds by the generation of an electrophile (Br^+) which is produced by the heterolytic cleavage KBr by an acidic catalyst. The Br^+ attacks the aromatic ring resulting in the formation of brominated products [6]. Heteropoly acids (HPAs) especially Keggin types HPAs are known to be excellent for acid-catalyzed and oxidative reactions catalysts. Heteropoly acids are polyoxometalates made up of heteropolyanions having metal-oxygen octahedral as the basic structural unit. The use of HPA as catalysts is important in the development of clean technologies, since it avoids the drawbacks of environmental pollution and prevents corrosion of the conventional technologies [7,8]. The disadvantage of bulk HPA as catalysts is their relatively low stability and surface area (1–10 m^2/g). To overcome these disadvantages, the HPA are usually immobilized on a suitable carrier that not only increases the available surface area and thermal stability but also improves the catalytic performance [9]. The catalytic activity of immobilized HPA depends on the HPA loading, the pretreatment conditions and the type of the supporting material. Acidic or neutral substances such as SiO_2 [10], active carbon [11], acidic ion-exchange resin [12], TiO_2 [13], MCM-41[14] zirconia [15,16], clay [17,18], SBA-15 [19,20] are suitable as supports. In this study, we have used heteropoly acids impregnated nanoparticles of nickel oxide as heterogeneous catalyst for the liquid phase bromination of phenol with KBr as the brominating source and H_2O_2 as the oxidant.

In this work, we have reported the preparation of ecofriendly solid acid catalyst immobilized onto nickel nanoparticle with an incipient wetness impregnation method in order to contribute towards clean technology. This composite was indicated a high performance in liquid phase bromination of phenols. Bromination of phenols was catalyzed by a composite of silicotungstic acid (STA) and nickel nanoparticle as heterogeneous catalyst. STA is the most commonly encountered heteropoly acid. It is a pale yellow solid with the chemical formula $H_4[W_{12}SiO_{40}]$. It is used as a catalyst in many chemical industries. The bromination of phenol is shown in Scheme 1.



Scheme 1. The bromination of phenol process

Experimental

Catalyst preparation

Silicotungstic acid was prepared by the method described in the paper [1]. At first, sodium tungstate (10 g) was dissolved in 40 mL of deionized water. Then, 0.1 M sodium meta-silicate was added to initial solution and mixture of reaction was refluxed at 80ºC under stirrer, then 16 mL of HCl 24% was added dropwise to the initial solution. The solution was extracted by diethyl ether, and then evaporated to dryness at room temperature. STA impregnated on nanoparticle of nickel oxide was prepared by sol-gel method. For this purpose, $NiCl_2.6H_2O$ (3 g, 0.0126 mol) was added to a 500 mL round bottom flask and dissolved in 140 mL of ethanol at room temperature. In another beaker, NaOH (1 g, 0.025 mol) was dissolved in 200 mL ethanol and the NaOH solution was added dropwise to the nickel chloride solution. The mixture of reaction was stirred at room temperature for 2 h. Then, the green gel obtained was filtered and washed with distilled water and ethanol. The precipitate obtained was dried at room temperature, yielding a green colored powder. Appropriate quantity of STA solution in 20 wt% was taken with 1 g of nanoparticles of nickel oxide in a beaker and heated at 80 ºC with continuous stirring till complete dryness. Then it was dried at 80 ºC for 8 h.

General procedure for bromination of phenol

The catalytic reaction was performed in a 20 mL round bottom flask which charged with 0.1 g of prepared catalyst, phenol (2 mmol), acetic acid (4 mL) and 2.2 mmol KBr. Then, 2.2 mmol H_2O_2 30% was added to the reaction mixture and stirred for 4 h at room temperature. Finally, the mixture of reaction was filtered and solid catalyst was washed with diethyl ether. The combined filtrates were washed with saturated sodium bicarbonate solution and the reaction product was extracted by ether. The obtained organic powder was dried over anhydrous magnesium sulfate. The products of reactions were analyzed by GC (Shimadzu GC-17 A) through capillary column.

Results and discussion

Characterization of catalyst

XRD patterns of the catalysts were obtained on a D/MAXrA (Rigaku) diffractometer with Cu Kα radiation (λ= 1.542A˚). The XRD pattern of heterogeneous catalyst, STA and nanoparticles of nickel oxide are shown in Figure 1. Intensity of some picks decreased in 3–10° which demonstrated STA successfully immobilized on nanoparticles of nickel oxide with sol–gel method. The Fourier transform infrared spectra (FT-IR) were recorded by a Perkin-Elmer system 2000 FT-IR spectrometer in the range 500-4000 cm^{-1} using the KBr disk technique shown in Figure 2. By comparing the FT-IR spectra, it was observed that four additional bands corresponding to STA at 785, 924 and 985 cm^{-1} were appeared. The obtained results of FT-IR spectra indicated the structure of STA retained after supporting on carrier. Electrostatic interaction between STA anion and hydroxyl group on surface of nickel oxide leads to immobilize the heteropoly acid on nanoparticle. The Optima 8000 ICP-OES spectrometer was used to determine heteropoly acid amount of tungsten in the catalysts. The results showed that 96% of the STA is adsorbed on the surface of the carrier.

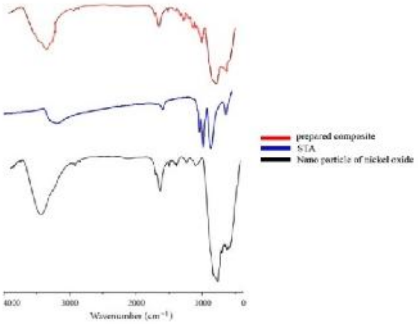


Figure 1. XRD patterns of prepared catalyst

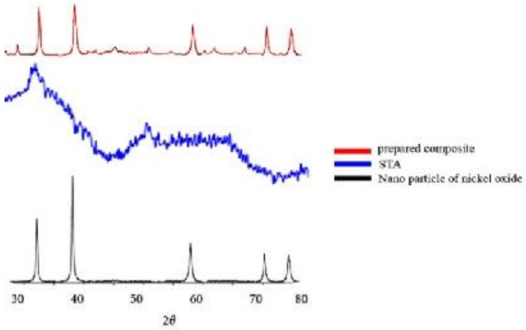


Figure 2. FT-IR spectra of prepared catalyst

Catalyst activity

The catalytic activity towards brominating of phenol using STA impregnated on nanoparticles of nickel oxide was summarized in Table 1.

Table1. Conditions applied to the bromination of phenol

Solvent	Reaction time(h)	catalyst (g)	amount of oxidant(mmol)	Yield[a] orto%	Yield para%
Acetonitrile	4	0.1	0.5	38	6
Acetic acid	4	0.1	0.5	35	6
Ethanol	4	0.1	0.5	29	4
Chloroform	4	0.1	0.5	15	2
Dichloromethane	4	0.1	0.5	12	0
Acetonitrile	2	0.1	0.5	35	5
Acetonitrile	4	0.1	0.5	38	6
Acetonitrile	6	0.1	0.5	42	9
Acetonitrile	8	0.1	0.5	55	11
Acetonitrile	10	0.1	0.5	55	10
Acetonitrile	8	0.5	0.5	34	7
Acetonitrile	8	1	0.5	55	11
Acetonitrile	8	1.5	0.5	60	11
Acetonitrile	8	2	0.5	61	11
Acetonitrile	8	1.5	1	70	12
Acetonitrile	8	1.5	1.5	78	14
Acetonitrile	8	1.5	2	83	11

(a): GC yield

In order to optimize the conditions, bromination of phenol was investigated by changing various parameters such as solvent, amount of oxidant, amount of catalyst and reaction time. The poor conversion was observed in the dichloromethane medium. According to the results, acetonitrile was selected as an optimum solvent with the most efficiency for this reaction. In the next step, the amount of catalyst was optimized. The results showed the greatest amount of product by adding 0.15 g of catalyst to the reaction mixture. Initially, with increase in the catalyst amount the percentage of conversion of phenol increases thereafter it remains almost constant. This may be due to the decrease in the total surface area available to reactant resulting from overlapping or aggregation of active sites. In the industrial process, the contact time between the reactant molecules has significant importance for practical application. Therefore, the reaction time was also evaluated. The results were also indicated that the yield of the reaction increased with time and attained best conversion about 6 h. This time was considered as optimal reaction time. Bromination reaction was investigated with various organic substrates such as phenol. The results of this study are shown in Table 2.

Table 2. Bromination of various organic substrates under optimal condition

Entry	Time(h)	Ortho product (%)
Phenol	8	83
2-Ethylphenol	8	86
2-Chlorophenol	8	80
Anisole	8	77
Aniline	8	91
2-Chloroaniline	8	79

The results showed that the presence of electron acceptor such as NO_2 substituents in the aromatic ring leads to decreases in the rate and reduces the efficiency of the bromination reaction. On the other hand, the presence of electron-donating substituents on the aromatic ring such as NH_2 leads to the increased speed and efficiency of the reaction. Recovery and reusability of the catalyst were studied; the results are showed in Figure 3. In accordance with the results after 5 cycles of recovery catalyst, the reaction yield is still higher than 70%.

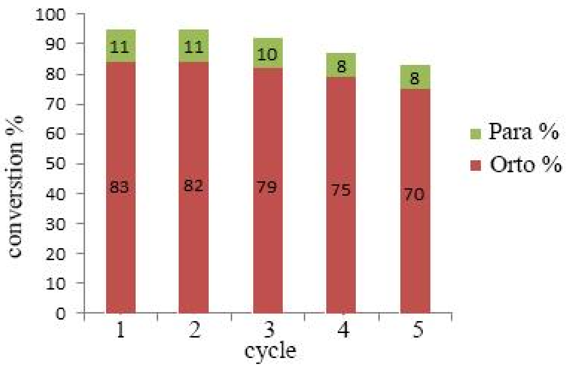


Figure 3. Recyclability of prepared composite in this reaction

Conclusion

In summary, STA anions were immobilized on nickel oxide nanoparticles with impregnation method and used to bromination of phenols. The obtained catalyst showed excellent catalytic activity and reusability. In order to optimize the conditions, bromination of phenol was investigated by changing various parameters such as solvent, amount of oxidant, amount of catalyst and reaction time. The catalyst is easily recoverable and can be reused several times without leaching or loss of activity.

Acknowledgements

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