

A Novel Method for the Preparation of Core-Shell Silica - 12-Tungstophosphoricacid Nanoparticles for *t*-Butylation of phenol

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Abstract— Tert-butylated phenols find many applications in industries. A variety of solid acid catalysts has been reported for the *t*-Butylation of phenol. However, the activity of this catalyst is susceptible to coke formation or poor activity. This paper reports the novelties of steam treated DTP included silica nanoparticle for the liquid phase alkylation of phenol with tert-butanol. The effect of various operating parameters was investigated in terms of conversion and selectivity for the desired product under mild conditions.

Keywords- alkylation; dodecatungstophosphoric acid; nanoparticle; tert-Butylation

I. INTRODUCTION

Tert-butylation of phenol is an industrially important reaction and the alkylated products are widely used for a variety of applications such as antioxidants, herbicides, insecticides, and polymers [1]. They are conventionally prepared by reacting phenol with pure isobutylene gas or C₄ fraction of naphtha using a liquid acid catalyst, which gives wide product distribution. In general, tert-butylation of phenols is carried out in a homogeneous medium using sulphuric acid, phosphoric acid, aluminium chloride-boric acid or boron trifluoride as a catalyst [2]. The use of conventional Friedel-Crafts catalysts gives rise to many problems concerning handling, safety, corrosion, and waste disposal. Therefore, considerable efforts have been made for the development of suitable heterogeneous solid acid catalysts [3]. Although many commercial ion exchange resins exhibit high activity for the tert-butylation of phenol and substituted phenols with isobutylene, their lower thermal stability limit their industrial application. Various solid acid catalysts have been reported in the literature for tert-butylation of phenols [4-8]. Most of the solid acid catalysts reported are active and the most important problem is the selectivity for the desired product [9].

Among the solid acid catalysts, heteropoly acids (HPAs) are promising one for Friedel-Crafts reactions. Among Keggin type HPAs, 12-tungstophosphoricacid (TPA) is thermally more stable and acidic than any other HPAs. Supported DTP catalyst is proved to be a highly active solid acid catalyst for various acid catalysed reactions [10]. But, as of now, few works are available on supported heteropoly acid catalyst for the tert-butylation of phenol [11-13]. Herein, we report a highly active catalyst based on 12-Tungstophosphoricacid (DTP) included into a silica nanoparticle for the *t*-Butylation of phenol.

II. EXPERIMENTAL

A. Preparation of DTP included silica nanoparticle

The modified version of DTP included silica nanoparticle was prepared by sol-gel technique followed by steaming. In a typical procedure, 30wt % DTP/SiO₂ was prepared by dissolving dodecatungstophosphoric acid (3 g) in DI (10ml) water. Tetraethoxysilane mixed with ethanol (24.3 g TEOS in 10 g EtOH) was dropped into the above solution under vigorous stirring. The solution turned into a transparent viscous gum-like liquid. The gel was subjected to vacuum evaporation at 70°C. Upon vacuum evaporation, the solution turned into a transparent sticky solid, which finally turned into transparent sugar-like cubes. The solid was dried in an air oven at 120°C for 6 hrs. The dried solid was steamed in an autoclave at 150°C for 6 hrs.

B. Characterization

Powder X-ray diffraction patterns were recorded using a Rigaku 2000 diffractometer equipped with a Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) from $2\theta = 2.5$ to 60° at a scan rate of $2^\circ/\text{min}$ using a step size of 0.04° . Morphology and particle size examinations of the samples were carried out using TEM (JEM-2010, 200kV). Nitrogen adsorption measurements were carried out at 77.4 K on a Micromeritics ASAP 2010 instrument. The nature of the acid sites of the catalyst sample was determined by Fourier transform infrared (FTIR) spectroscopy with chemisorbed pyridine. The vapor phase adsorption of pyridine as probe molecule was adopted to find out the acidity of catalyst samples [14]. The nature of acid sites was characterized on the basis of IR spectral data of pyridine adsorbed catalyst samples. The strength of acidic sites was determined by differential scanning calorimetric studies.

C. Catalytic activity studies

All experiments were carried out in a 100 ml round bottom flask. Phenol (150 mmol), tert-butyl alcohol (10 mmol) and 0.15 g catalyst was added and heated in oil bath to a given temperature. The products formed were analyzed by GC and are confirmed by GC-MS.

III. RESULTS AND DISCUSSION

A. Surface area measurements

The surface area of the unsteamed 30 wt % DTP/SiO₂ was only 27 m²/g; whereas after steaming, it increased drastically up to 10 times, i.e. the surface area of 30 wt % DTP/SiO₂ was increased to 277 m²/g. The increase in surface area was explained as follows: During the steaming process, the solubility of polymeric silicate species increases due to the presence of steam at high pressure under acidic heteropoly anion condition. The local concentration domains of silicate ions increases, which deprives their growth. Thus, a steamed sample will have a large number of small particles. It is possible that during this process, the DTP dissolved and distributed more uniformly on the silica nanoparticles. Similar observation was also noticed in the vapour phase transport method for the zeolite synthesis [15].

B. XRD

The XRD patterns of 30 wt % DTP/SiO₂ sample before and after steaming are shown in Fig. 1.

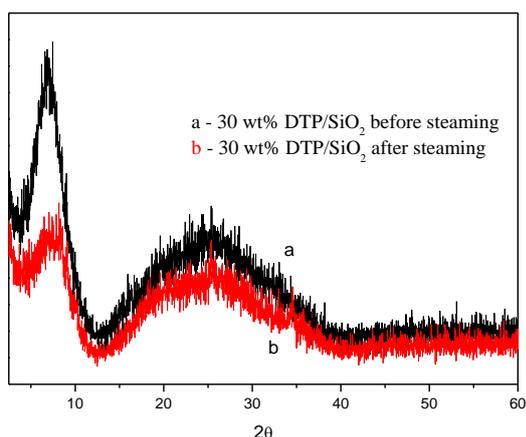


Figure 1. XRD patterns of 30 wt % DTP/SiO₂ (a) before steaming (b) after steaming.

The XRD pattern of the sample is similar to that of silica except a broad peak located at 2θ between 3 - 8°. It is more likely that this low angle very broad peak is due to the scattering of small particles. The XRD result confirms that there is no free DTP particle before and after steaming.

C. TEM

TEM micrographs of 30 wt % DTP/SiO₂ sample prepared before and after steaming are reported in Fig. 2. As seen in the micrograph, steaming clearly leads to a decrease of the size of silica particles and an increase of the DTP particles sizes. This means and confirms that after steaming the DTP particles are coated uniformly on the surface of the much smaller silica particles, thus forming SiO₂/DTP core-shell nanoparticles.

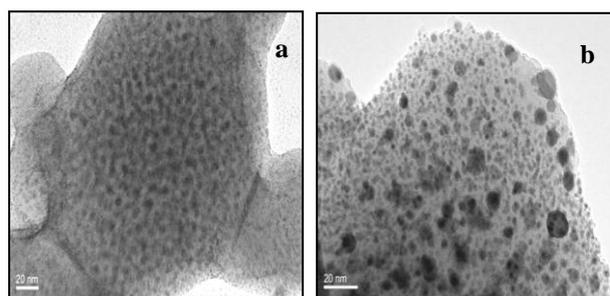


Figure 2. TEM image of 30 wt % DTP/SiO₂: (a) before steaming (b) after steaming.

D. Acidity measurements

The IR bands recorded for pyridine adsorbed on the catalyst samples are shown in Fig. 3. The absorption bands at 1630 cm⁻¹ indicate the presence of Bronsted acid sites. The intensity of the absorption bands at 1630 cm⁻¹ increased after steaming. Further, the strength of acid sites was confirmed by DSC analysis. The DSC thermograms of pyridine desorption from the catalyst indicates that after steaming the heat of desorption of pyridine increased from 300 to 720 J/g. This confirms that steaming of silica included heteropoly acid enhanced the strength of Bronsted acid sites.

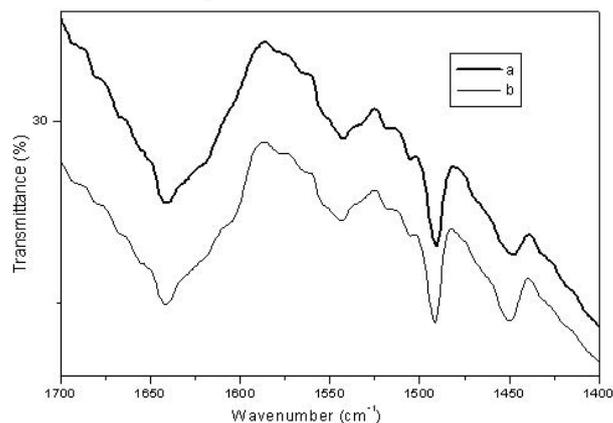
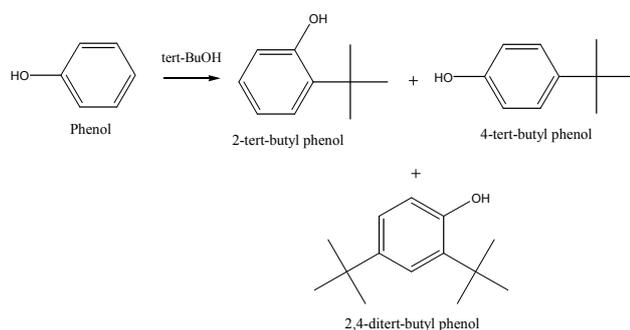


Figure 3. FTIR spectra of 30 wt % DTP/SiO₂ exposed with pyridine (a) before steaming and (b) after steaming.

IV. ALKYLATION OF PHENOL WITH TERT-BUTYL ALCOHOL

Alkylation of phenol with tert-butyl alcohol was carried out using the supported DTP catalysts. This reaction leads to the formation of 4-tert-butyl phenol (4-TBP) as the major products along with significant amount of 2-tert-butyl phenol (2-TBP). Under specific conditions negligible amount of 2,4-di-tert-butyl phenol (2,4-DTBP) was obtained. The reaction scheme is represented in Scheme 1. Preliminary studies were performed to optimize reaction parameters such as, reaction temperature; phenol/ tert-butyl alcohol molar ratio and catalyst quantity using the steamed 30 wt % DTP/SiO₂ catalyst.



Scheme 1. Tert-butylation of phenol.

A. Catalytic activity of un-steamed and steamed DTP/SiO₂ catalyst

The fresh and steamed 12-tungstophosphoric acid included on silica nanoparticles were tested for tert-butylation of phenol. The fresh 12-tungstophosphoric acid included on silica nanoparticles was found to be less active (44 % conversion). The steam treatment tremendously increased the catalytic activity of 30 wt % DTP/SiO₂ catalyst sample (95.6 % conversion) and is due to the drastic increase of the surface area and Bronstead acid strength.

B. Effect of catalyst quantity

The effect of catalyst quantity was studied over a range of 0.05–0.2 g for alkylation of phenol with tert-butyl alcohol at 80 °C. The conversion and selectivity are presented in Table I.

TABLE I. EFFECT OF CATALYST AMOUNT ON ON THE ALKYLATION OF PHENOL WITH TERT-BUTYL ALCOHOL

Catalyst Weight (g)	Conversion of tert-butyl alcohol (%)	Selectivity (%)		
		4-TBP	2-TBP	2,4-DTBP
0.05	67	95	4.5	0.5
0.10	84.0	95.8	3.7	0.5
0.15	95.6	98.5	0.1	0.4
0.20	97.8	98	1.6	0.4

Conditions: catalyst, steamed DTP/silica; molar ratio of phenol: tert-butyl alcohol, 15 : 1; reaction temperature, 80 °C.

The conversion of tert-butyl alcohol was found to increase with increase in catalyst amount, which is due to the proportional increase in the number of active sites and the increase becomes less significant beyond 0.15 g. This indicates that beyond 0.15 g, the additional active sites do not increase the adsorption of reactants at a given concentration and so the conversion of tert-butyl alcohol does not increase much.

C. Effect of temperature

The activity of the steamed 12-tungstophosphoric acid included on silica nanoparticles for tert-butylation of phenol was tested at different temperatures. The results presented in Table II indicate that the conversion was increased with

increasing temperature till 80 °C and thereafter remained constant.

TABLE II. EFFECT OF TEMPERATURE ON THE ALKYLATION OF PHENOL WITH TERT-BUTYL ALCOHOL

Temperature (°C)	Conversion of tert-butyl alcohol (%)	Selectivity (%)		
		4-TBP	2-TBP	2,4-DTBP
40	54.8	97.9	1.7	0.4
60	86.5	99.0	0.5	0.5
80	95.6	98.5	0.1	0.4
100	95.8	97.2	2.2	0.6

Conditions: catalyst, 0.15 g of steamed 30 wt % DTP/SiO₂; molar ratio of phenol: tert-butyl alcohol, 15 : 1.

D. Reusability of the catalysts

To investigate the efficiency of the newly developed steamed 30 wt % DTP/SiO₂ catalyst, it was reused three times. For this, the used catalyst was centrifuged, washed with CH₂Cl₂ and subsequently dried at 120°C for 6 hrs before being reused in subsequent batches. It was found that there was no loss of the catalytic activity up to three runs. Thus it is concluded that DTP was chemically adsorbed on the catalyst surface, hence, the catalyst was reusable.

V. CONCLUSIONS

The present work demonstrates the alkylation of phenol by tert-butyl alcohol using DTP/silica nanoparticle catalysts. The reaction parameters such as, catalyst quantity and reaction temperature were optimized. Under the optimum reaction conditions (80°C, a phenol by tert-butyl alcohol mole ratio of 1:5, 0.15 g catalyst), the steamed DTP/ Silica nanoparticles gave 95.6 % conversion of tert-butyl alcohol. We believe that the present approach of preparing this catalyst may be extended to the fabrication of monolithic stirrer reactor which was proven to be a versatile system for fine chemicals production in batch mode. Moreover, the steamed DTP/silica nanoparticle catalyst is considered as a potential replacement for conventional Lewis acid or mineral acid catalysts for alkylation of phenol with tert-butyl alcohol.

ACKNOWLEDGMENT

Financial support from the Ministry of Higher Education via the Taiwan-India collaboration research program, in addition to the basic funding provided by the Lunghwa University of Science and Technology is gratefully acknowledged.

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