

# Catalytic performance of Preyssler heteropolyacid, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ in liquid phase alkylation of phenol with 1-octene

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## Abstract

Under mild conditions a liquid phase alkylation of phenol with 1-octene was studied in the presence of Preyssler catalyst,  $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ . This polyanion with high hydrolytic stability (pH 0–12), thermal stability and high acidic strength shows great activity. The effects of various parameters on the yield of product, including catalyst type, reactant molar ratio, solvent type and reaction time were studied. Comparison between Keggin type heteropolyacids,  $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$ ,  $\text{H}_6[\text{PMo}_9\text{V}_3\text{O}_{40}]$  and Wells–Dawson,  $\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$  with Preyssler's anion shows that the latter reacts better than the other studied heteropolyacids and without any degradation of the structure.

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## 1. Introduction

Long-chain (>C8) alkyl phenols are used in the industry in the manufacture of surfactants, as antioxidants and as additives in lubricants and plastics.

These are typically manufactured by the alkylation of phenol with the corresponding long-chain olefins or alcohols over acid catalysts such as  $\text{BF}_3$  and ion exchange resins [1]. Several catalysts have been reported for *t*-butylation of phenol which include Lewis acids such as  $\text{AlCl}_3$  and  $\text{BF}_3$  [2], Bronsted acids such as  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ , HF and  $\text{HClO}_4$  [3], cation exchange resins [4], porous materials [5–8], supercritical and near supercritical water [9] and ionic liquids [10]. The major drawbacks of homogeneous catalysts are their hazardous nature and tedious procedure involved in the separation of catalyst from the reaction mixture after completion of the reaction. In order to overcome the aforementioned drawbacks, attention has been paid to make use of molecular sieves as catalyst [11–14]. Zhang et al. [7] stud-

ied *t*-butylation of phenol with *tert*-butyl alcohol (TBA) over zeolite HM. Although zeolites are advantageous, the use of zeolites has been restricted in recent years owing to its limitation in processing bulky molecules.

Heteropolyacids (HPA) have witnessed rapid growth in the last decade as solid acid catalyst [15–17]. Polyoxometalates have been chosen as catalyst because of their easy availability and extreme stability in solution as well as in solid state. HPAs have several advantages that make them economically and environmentally attractive. They are good acid catalysts in homogeneous medium. They catalyze a wide variety of reactions in homogeneous phase offering strong option for efficient and cleaner processing compared to conventional mineral acids [18–22].

Until now, most of the research concerning catalytic properties of HPAs has been carried out using, Keggin structure and its derivatives as defect, mixed addenda, supported, etc. In the recent years, the interest in other HPAs, has been growing in the literature. As a part of a research project to develop environmentally friendly catalysts, we have recently applied the Preyssler HPA catalyst to various

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reactions [23–25]. However, the capability of this catalyst still has been largely overlooked [26]. In our opinion, advantages such as: high hydrolytic stability (pH 0–12), which demonstrates its functionality over a wide range of pH, high thermal stability and having a large number of acidic protons (14) along with exclusive structure for Preyssler's anion are outstanding and make it a good candidate for further studying. This polyanion consists of a cyclic assembly of five  $\text{PW}_6\text{O}_{22}$  units; each derived from the Keggin anion,  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ , by the removal of two sets of three corner shared  $\text{WO}_6$  octahedra [27].

In this paper we present a liquid phase alkylation of phenol with 1-octene over Preyssler heteropolyacid catalyst,  $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ , and compare the catalytic performance of this catalyst with other heteropolyacids such as  $\text{H}_5[\text{PMO}_{10}\text{V}_2\text{O}_{40}]$ ,  $\text{H}_6[\text{PMO}_9\text{V}_3\text{O}_{40}]$  and Wells–Dawson,  $\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$ . The influence of process variables such as reactant molar ratio, reaction time and catalyst type on the reaction have also been investigated.

## 2. Experimental

The reaction products were identified by GC–mass and IR. IR spectra were recorded as KBr disc on the FT-IR Bruker Tensor 27 spectrometer. Mass spectra were recorded on MS 5973 network mass selective detector. All the yields were calculated from isolated products, and GC was used to establish their purities.

All compounds were purchased from Merck Company. Yields are based on GC/mass analysis using Agilent 6890 GC system Hp-5 capillary 30 m  $\times$  530  $\mu\text{m}$   $\times$  1.5  $\mu\text{m}$  nominal.

### 2.1. Alkylation of phenol with 1-octene

The reactions were carried out in a flask (25  $\text{cm}^3$ ) using 1 mmol of phenol and 4 mmol of 1-octene and 0.01 mmol of catalyst, at atmospheric pressure. The mixture was then refluxed for appropriate reaction time. The progress of the reaction was monitored by thin layer chromatography (TLC) using THF as eluent.

After completion of the reaction, the catalyst was filtered. To the filtrate diethyl ether (15 mL) was added. The mixture then washed with 5%  $\text{NaHCO}_3$  (10 mL) and brine (2  $\times$  5 mL) successively, and dried over  $\text{MgSO}_4$  and filtered. The solvent was evaporated under reduced pressure and further purification was obtained by flash chromatography.

## 3. Result and discussion

The catalytic alkylation of phenol with 1-octene by Preyssler's anion as the catalyst is reported. The reactions were carried out in various solvents such as dichloromethane, chloroform, THF and solvent free conditions.

The reaction products were identified by GC–mass and IR spectra. Experiments in the absence of the catalyst yielded no substantial quantity of product.

As for the solvent effects on the reaction, the different reaction behaviors may originate from differences in reactants concentration and reaction temperature. To distinguish them the solvent free reactions were refluxed at boiling point of indicated solvents (Table 1).

As shown in Table 1 the best results in terms of phenol conversion and reaction time have been achieved in solvent-free system. Solvent influence on the reaction rate and selectivity was discerned to depend on competitive adsorption, rather than reflect a direct kinetic solvent effect. Our experiments in the presence and absence of solvent show that two things occur in the presence of the solvent: the reaction is slower, and the final yield is lower. While the former may be attributed to lower reactant concentrations, the latter indicates that the solvent enhances catalyst deactivation, possibly by facilitating the approach of 1-octene to the catalyst surface. Consequently, the best conversion was achieved by using no solvent. By using THF, dichloromethane and chloroform as a solvent, GC analysis showed the selectivity for para isomer did not change and in all conditions para isomer were obtained as single products.

### 3.1. Product selectivity

The alkylation of phenol with 1-octene over the heteropolyacids catalysts resulted in the formation of the mono-alkylated product. In the absence of a catalyst, the reaction did not proceed. The reaction between phenol and 1-octene over the catalysts produced only carbon alkylated (C-alkylated) product. Catalytic activity and selectivity for the reaction under the different condition are listed in Table 2. From Table 2, it is seen that product selectivity to *p*-isomer over catalyst is very high. In general, the observed selectivity was 100%. Activities of the catalysts for the reactions were evaluated by the conversion of phenol.

### 3.2. Effect of the catalyst type

In order to compare the Keggin type and Dawson catalysts with Preyssler catalyst in the alkylation of phenol with 1-octene, we selected the Keggin types  $\text{H}_5[\text{PMO}_{10}\text{V}_2\text{O}_{40}]$ ,

Table 1  
Alkylation of phenol, in the presence of  $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ , refluxing in different solvents (5 mL)

Entry	Solvent	Temperature ( $^{\circ}\text{C}$ )	Phenol conversion <sup>a</sup> (%)
1	THF	88	56
2	Solvent free	88	63
3	$\text{CHCl}_3$	61	44
4	Solvent free	61	51
5	$\text{CH}_2\text{Cl}_2$	40	28
6	Solvent free	40	37

Catalyst weight = 0.5 g; phenol:1-octene (feed ratio) = 1:4; reaction time = 8 h.

<sup>a</sup> Yields analyzed by GC.

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