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Short communication

# $H_{3+x}PMo_{12-x}V_xO_{40}$ (heteropolyacids)-catalyzed regioselective nitration of phenol to *o*-nitrophenol in heterogeneous system

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## Abstract

Mononitration of phenol was examined, using nitric acid in the presence of heteropolyacids $H_{3+x}PMo_{12-x}V_xO_{40}$ ($x = 1$–$3$) in different solvents. In all cases heteropolyacid with $x = 3$ gave the highest yield by using carbon tetrachloride as solvent. The effects of various parameters such as concentration of phenol, solvent, temperature and time of reaction have been studied.

*Keywords:* Vanadium(V)-substituted polyoxomolybdates; Heteropolyacid; Catalyst; Nitration; Phenol

## 1. Introduction

Nitration of aromatic compounds is widely used in organic syntheses and in industrial applications [1]. The most important nitro aromatic compounds in environmental chemistry are nitro-PAHs and nitrophenols [2].

The nitration of phenol is a fundamental processes, because nitrophenols are important intermediates for the manufacture of drugs and pharmaceuticals. Among these compounds *ortho*-nitrophenol (*o*-nitrophenol) is an important starting material used in multiple step synthesis of valuable compounds [3]. A variety of nitrating agents have been employed in nitration of phenols but usually these nitration reactions are not selective. Impregnated alumina and silica with $N_2O_4$ [4], $NaNO_3$ in a two phase system (water–ether) in the presence of catalytic amount of $La(NO_3)_3$ [5], an ionic complex of $N_2O_4$ with 18-crown-6 [6], ceric ammonium nitrate in the presence of $NaHCO_3$ [7], metal nitrates [8], nitronium tetrafluoroborate [9], zirconyl nitrate [10], have been used as nitrating agents for phenols.

Meanwhile zeolites-based solid acid catalysts [11], iron loaded sulfated titania catalyst [12], claycop (copper(II) nitrate supported on K10-Montmorillonite) [13], ionic liquids [14], and TBAB as transfer catalyst [15] have been used as catalyst for regioselective nitration of phenols.

Considering these reactions and with the cause of environmental concerns, there is still a good scope for research towards finding green and eco-friendly catalysts for regioselective nitration of phenols.

Heteropolyanions are polymeric oxoanions formed by the condensation of more than two different mononuclear oxoanions [16]. The use of heteropolyacids, HPAs, as catalyst for fine organic synthesis processes is developing and synthesis of antioxidants, medicinal preparations, vitamins and biologically active substances has been reported by using them [17]. In addition, these catalysts are very important for industries related with fine chemicals as flavors, pharmaceutical and food industries [18]. Among the numerous heteropolyacids, heteropolymolybdates and tungstates related to the Keggin structure have received much attention [19,20].

Recently, we have investigated various catalytic performances of heteropolyacids in different reactions [21]. In seeking to develop new synthetic methods for organic compounds by using heteropolyacids, in the present work, the performance and applicability of three kinds of vanadium(V)-substituted polyoxomolybdates such as $H_4PMo_{11}VO_{40}$, $H_5PMo_{10}V_2O_{40}$, and $H_6PMo_9V_3O_{40}$ has been studied for regioselective nitration of

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phenol under mild experimental conditions. We have found that $H_6PMo_9V_3O_{40}$ in carbon tetrachloride as solvent afforded the regioselective *o*-nitrophenol in excellent yield.

## 2. Results and discussion

Nitration of phenol with nitric acid in different solvents was explored using vanadium(V)-substituted polyoxomolybdates, $H_{3+x}PMo_{12-x}V_xO_{40}$ ($x = 1–3$). Hetropolyacids with $x = 1–3$ catalyze the nitration of phenol leading to *o*-nitrophenol as major product depending on the solvent of the reaction. In a systematic study and aimed work, in the presence of all of the catalysts, the reaction has been examined with different solvents and then in the solvent of choice. The effects of the reaction temperature have also been studied. At the next stage, in the best solvent and temperature the effects of the reaction time have been studied. Finally in optimum conditions the effects of the concentration of phenol has been checked.

### 2.1. *Effect of the solvent*

The nitration of phenol at reflux temperature was carried out using various common solvents such as $CCl_4$, $CH_2Cl_2$ and $CHCl_3$. The results are shown in Table 1. With using all of the catalysts the highest yield of *o*-nitrophenol was obtained with $CCl_4$ as solvent. In addition, the time required for completion of the reaction was found to be less in $CCl_4$. GC analysis showed by using dichloromethane and chloroform as a solvent, the selectivity for *o*-nitrophenol is lower and a mixture of 2-nitro- and 2,4-dinitrophenol are obtained. The highest yield of 100% and selectivity 100% for *o*-nitrophenol in carbon tetrachloride indicates the influence of the solvent on the yield of reaction.

Because of large negative charge of polyoxoanions, all of the HOMOs and LUMOs of them have very high energy levels. These highly charged heteropolyanions do not exist in the gas phase and that the external field generated by the solvent is crucial to stabilize them. With regard to the heteropolyanions which are reducible easily and is required in catalytic reactions, the energy of the LUMO must be sufficiently low to accept the electrons in catalytic reactions. The solvent molecules can place these molecular orbitals at the appropriate level. As shown in Table 1, the solvent effects change in parallel to the charges of the anions. The greater negative charge lead to the greater solvent effects and finally the higher yields. It is suggested that the solvent effects are dominated by the interactions of the polarized polyanions with the solvent, to place the molecular orbitals at the appropriate level and or to lower the activation energy. Apparently this effect is higher for $CCl_4$.

Table 1
Catalytic nitration of phenol in the presence of different solvents

| Solvent | Catalyst | Temperature (°C) | Time (h) | Yield (%)[a] |
|---|---|---|---|---|
| $CCl_4$ | $H_4[PMo_{11}VO_{40}]$ | Reflux | 5 | 93 |
| $CH_2Cl_2$ | $H_4[PMo_{11}VO_{40}]$ | Reflux | 5.5 | 82 |
| $CHCl_3$ | $H_4[PMo_{11}VO_{40}]$ | Reflux | 6 | 50 |
| $CCl_4$ | $H_5[PMo_{10}V_2O_{40}]$ | Reflux | 2.5 | 96 |
| $CH_2Cl_2$ | $H_5[PMo_{10}V_2O_{40}]$ | Reflux | 3 | 58 |
| $CHCl_3$ | $H_5[PMo_{10}V_2O_{40}]$ | Reflux | 4 | 41 |
| $CCl_4$ | $H_6[PMo_9V_3O_{40}]$ | Reflux | 1.5 | 100 |
| $CH_2Cl_2$ | $H_6[PMo_9V_3O_{40}]$ | Reflux | 1.5 | 87 |
| $CHCl_3$ | $H_6[PMo_9V_3O_{40}]$ | Reflux | 2 | 85 |

[a] Yields analyzed by GC.

### 2.2. *Effect of the catalyst*

The hetropolyacids of the series $H_{3+x}PMo_{12-x}V_xO_{40}$ ($x = 1–3$) showed good to excellent catalytic behaviors in the nitration of phenol in $CCl_4$, $CH_2Cl_2$ and $CHCl_3$. The results are shown in Table 1. $H_6$ $PMo_9V_3O_{40}$ catalyzes efficiently the formation of *o*-nitrophenol giving a total yield of 100% in $CCl_4$. The yield with this catalyst was found to be decreased from 100% to 85% when the solvent was changed from $CCl_4$ to $CHCl_3$ (entries 7–9). In addition, $H_4PMo_{11}VO_{40}$ and $H_5PMo_{10}V_2O_{40}$ gave a total yield 93% and 96% in $CCl_4$, respectively (entries 1 and 4). In another word, the activities of the $H_{3+x}PMo_{12-x}V_xO_{40}$ ($x = 1–3$) catalysts in the nitration of phenol in $CCl_4$ were found to decrease in the following order: $H_6PMo_9V_3O_{40} > H_5PMo_{10}V_2O_{40} > H_4PMo_{11}VO_{40}$. Many properties of the heteropoly compounds in solution depend on the concentration, the reaction time, the reaction temperature, the solvent type, the structure of catalyst, the pH value of the solution, and other factors.

The Keggin anion have an assembly of 12 corner-shared octahedral $MoO_6$ from trimetallic groups $[Mo_3O_{13}]$ around a heteroatom tetrahedron $PO_4$ [22]. The introduction of vanadium(V) into the Keggin framework of $[PMo_{12}O_{40}]^{3-}$ is beneficial for catalysis reactions [23]. Usually positional isomers are possible and coexist when two or more vanadium atoms are incorporated into the Keggin structure (for example 5 and 13 isomers for $x = 2$ and 3, respectively) [24]. Studies on these isomers in catalytic reactions indicate that different isomers cause to show different reactivities [25].

With respect to the catalytic performances for these catalysts and the overall effects of all isomers, for synthesizing of them, we cannot control the reaction conditions to synthesis of positional vanadium-substituted isomers separately, revealing the relationship between the structures of $H_{3+x}PMo_{12-x}V_xO_{40}$ ($x = 1–3$) and hence study of their catalytic activity, is difficult.

However, because the metal substitution may modify the energy and composition of the LUMO and redox properties, for mentioned heteropolyacids with different charges, the energy and composition of the LUMOs have significant effects on the catalytic activity [26]. Substitution of vanadium ions into the molybdenum framework stabilize the LUMOs because these orbitals derive, in part from vanadium d-orbitals which have been assumed to be more stable than those of molybdenum and tungsten [27].

The abundance of different isomers may also play an important role in catalytic performance. In addition, different positional Mo atom(s) substituted by the V atom(s) in $[PMo_{12}O_{40}]^{3-}$ may create different vanadium chemical environments, thus causing these catalysts to exhibit varying catalytic performances.