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Feature Article

Catalytic way of transforming 2,3-dimethylphenol to *para*-quinone with the use of vanadium-containing heteropoly acids

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ABSTRACT

2,3-Dimethyl-*p*-benzoquinone (2,3-Me_2BQ) is a valuable chemical that is applied as a soft oxidizing and dehydrogenating agent and also as a synthon in preparing different complex products including pharmaceutical and biochemical substances. Keggin- and modified-type aqueous solutions of Mo-V-phosphoric heteropoly acids (Mo-V-P HPAs) with the gross compositions $H_{3+x}PMo_{12-x}V_xO_{40}$ (HPA-x) and $H_aP_zMo_yV_{x'}O_b$ (HPA-x'), respectively, possessing high oxidation potential and simplicity of regeneration can serve as effective soft oxidants for obtaining such *para*-quinone from 2,3-dimethylphenol (2,3-Me_2P). The synthesized HPA catalysts with different vanadium content were characterized by a number of analysis techniques, such as ^{31}P and ^{51}V NMR spectroscopy, potentiometry, titrimetry, and pH measurement. It was found that the predominant formation of 2,3-Me_2BQ instead of corresponding diphenoquinone (DPQ) at one-electron oxidation is achieved by a consecutive optimization of reaction conditions, the most important among them being organic solvent and molar ratio of vanadium(V) to substrate. As was shown, the substitution of HPA-x by HPA-x' allows one to increase the quinone selectivity and to decrease the optimal molar ratio of vanadium(V) to substrate. The highest yield of the desired quinone (97%) at total substrate conversion was obtained by using the biphasic water-benzene system at molar vanadium(V) to substrate ratio of 12. The temperature of 50 °C and an inert atmosphere were established to be the optimal reaction conditions. The aqueous HPA-10′ solution including the highest content of VO_2^+ ions proved to be the most efficient catalyst among investigated HPAs. Carrying out catalyst regeneration at a separate stage provides the preservation of its activity and selectivity at the initial level for at least ten cycles.

1. Introduction

Developing the processes of industrial multistage low-tonnage production of organic substances is an important area which intensifies nowadays all over the world [1,2]. Being potential products and ‘platform molecules’ in this area, quinones can serve as one- or two-electron acceptors and also participate in a wide range of biological redox processes, such as NAD- and FAD-dependent reactions, processes of photosynthetic and respiratory energy transduction, and in reactions catalyzed by a group of enzymes designated quinoproteins [3]. Due to the ability of quinones to transfer both electrons and protons, they also play an important biochemical role in understanding electron and proton movement.

2,3-Dimethyl-*p*-benzoquinone (2,3-Me_2BQ) is a valuable chemical which is applied as a sensitizer in photorefractive systems and amperometric sensors and as a soft oxidizing and dehydrogenating agent [4]. It is as well a very promising substrate for producing various medical and physiologically active substances. Owing to the presence of reactive C=C and C=O sites in the structure, 2,3-Me_2BQ may enter into diverse reactions including amination, acylation, alkylation and arylation as well as cycloaddition [5]. It allows one to apply this compound as useful synthon for synthesis of substances with antiparasitic [6,7], anticancer [8], and antioxidant [9–11] activities (Fig. 1). However, under conditions of redox processes, quinones and hydroquinones have no sufficient stability. As a result, the task of selective synthesis of benzoquinones has certain difficulties and requires of developing new methods for their preparation including environmentally safe catalytic technologies.

Selective oxidation of phenols is one of the most valuable reactions for preparing quinones with a simple structure, and a variety of different methods has emerged to date [4]. Previously, much attention has been paid on developing effective oxidizing systems on the basis of metal salts [12,13], transition metal complexes [14,15], oxide catalysts [16–18], microporous and mesoporous heterogeneous catalysts [19–24], with some of them showing excellent activity in oxidation of phenols. However, the insufficient stability and low activity at reusing

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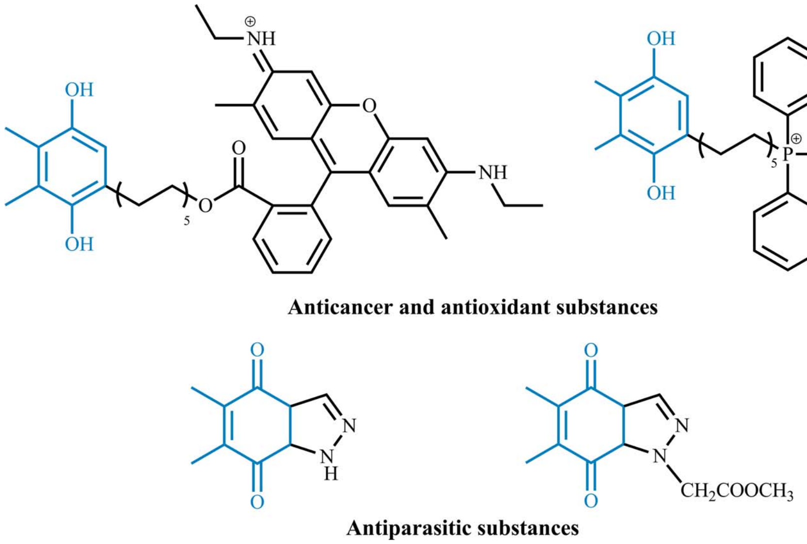

Fig. 1. Examples of valuable compounds obtained from 2,3-Me_2BQ.

along with hard regeneration conditions of these catalysts have limited their commercialization. The out-of-date processes based on oxidizing substituted anilines with MnO_2/H_2SO_4 at 10 °C or $Na_2Cr_2O_7/H_2SO_4$ at 20 °C are still used for preparing quinones [25]. As a consequence, further improvement of developed processes or investigation of alternative catalysts is required in this area.

Polyoxometalates (POM) are an extensive class of isopoly and heteropoly compounds, the properties of which can change broadly depending on elemental composition, the number of atoms in inorganic framework, relative position of atoms and their binding method, and also a counterion [26]. As a result, a large number of POMs currently exists, but only some of them are used in practice [27].

Today, the catalytic processes based on applying heteropoly (HP) compounds are an actively developing field of investigations [28–31]. Among HP-compounds used in oxidative and/or acid catalysis, the mixed-addenda Mo-V-phosphoric heteropoly acids (Mo-V-P HPAs, Fig. 2) attract significant attention as perspective oxidative [32–37] and bifunctional catalysts [38,39]. The interest of investigating such HP-compounds in catalysis has considerably increased lately due to the accumulation of data concerning their properties (especially owing to information dissemination on their reversible oxidability and simplicity of regeneration [40,41]). However, the solution both the general problems of this class of compounds (e.g. stability of catalysts) and the particular issues of their application for improvement of specific catalytic processes requires of extending investigations in this area.

In this work we investigated the synthesis of 2,3-Me_2BQ by oxidation of corresponding 2,3-dimethylphenol (2,3-Me_2P). The key to realize this reaction as the efficient catalytic one consists in applying catalysts possessing both a high oxidative ability and a possibility to rapid electron transfer. The shifting from acidic properties which are typical for all HPA groups to redox dominance due to the introduction into molybdenum-oxygen framework of vanadium(V) atoms (V^V) allows us to consider the aqueous Mo-V-P HPA solutions with Keggin $H_{3+x}PMo_{12-x}V_xO_{40}$ (HPA-x) and modified $H_aP_zMo_yV_{x'}O_b$ (HPA-x') gross compositions as promising homogeneous oxidative catalysts that can be used as soft oxidants for converting various organic compounds. Previously, we showed that this kind of catalysts exhibits excellent efficiency in some transformations including oxidation of trimethylphenol [42] and hydrolytic oxidation of cellulose [43]. At that, the choice of oxidant determines the efficiency and the practicality of systems, and molecular oxygen is regarded as a 'greenest oxidant'. This offers the significant opportunities for clean synthesis of fine and special chemicals [44].

This work is aimed at studying the effect of the composition of aqueous Mo-V-P HPA solutions and their oxidative properties as well reaction conditions on reaction time and product distribution during 2,3-Me_2BQ synthesis by oxidizing 2,3-Me_2P in order to obtain the maximal quinone selectivity and to ascertain the general patterns of this reaction. The major problem limiting the utility of homogeneous catalytic processes is the well-known difficulty in catalyst recovery and recycling. In our work we used a biphasic water-organic system that enables us to overcome the separation problem.

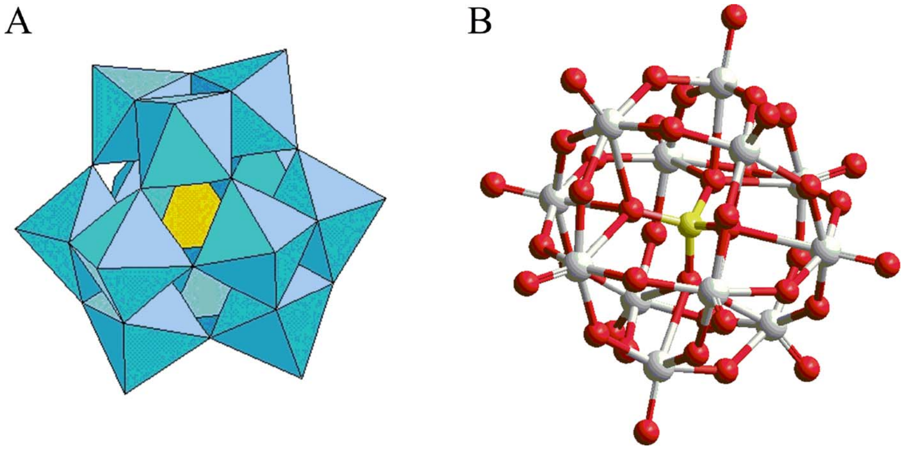

Fig. 2. Polyhedral (A) and component-bonding (B) models of α-Keggin polyoxoanion with general composition $[PM_{12}O_{40}]^{3-}$, M – structure-forming metal (Mo^{VI}, V^V).