Molybdovanadophosphate Heteropolyacid as Catalysts for Oxidation of Alkyl Substituted Phenols and Naphthols to Corresponding Quinones

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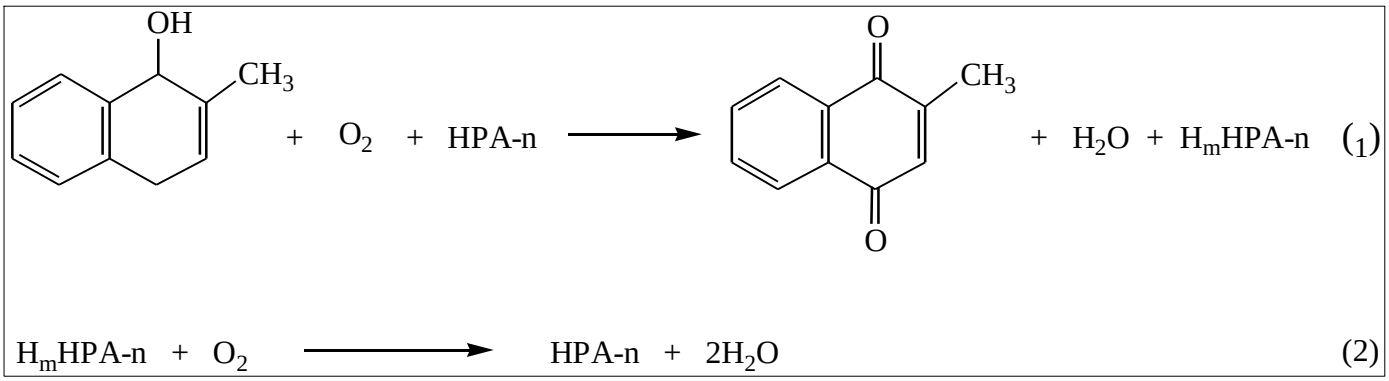
The oxidation of 2-methyl-1-naphtole (2MN1) to menadion (MD) (process A) is of practical importance as a step in the industrial production of vitamin K_3. Although there are many ways of doing this, the most of them are based on non-catalytic oxidation 2MN1 by chromium trioxide, in consequence of great amount of ecologically harmful wastes are forming. Therefore the most attractive methods are catalytic oxidations, which use clean and inexpensive oxidants especially dioxygen and hydrogen peroxide. Several catalysts can be used for the oxidation of 2MN1 by dioxygen. However, some of them exhibit a very low activity, while the others, due to the presence of oxidizable ligands, are not stable enough to sustain the oxidation for a long period despite their high activity.

In the present work we have used molybdovanadophosphoric heteropolyacids as catalysts for oxidation reaction. Heteropolyacides generally of the Keggin structure, $H_{3+n}PMo_{12-n}V_nO_{40}$ (HPA-n, n=1-8) have been found to be active homogeneous catalysts for the oxidation of 2MN1 by O_2. In the presence of these catalysts the process proceeds smoothly in mild conditions to yield MD as a main product (1). The reaction includes the stoichiometric oxidation of the phenol by HPA-n in a two-phase system and inert atmosphere and the reoxidation of the reduced HPA-n with O_2 in a separate step (2). MD yields with high selectivity (80-85%), without any harmful wastes.



Recently we also applied the similar catalysts for the anaerobic oxidation of 2,6-dimethylphenol (DMP) to 2,6-dimethyl-p-benzenequinone (DMQ) (process B). This substance is known to be the semi-product in the numerous syntheses of compounds showing a physiological activity. For example, DMQ may be used for preparing of trimethylbenzoquinone (TMQ), which is known to be an important step of industrial production of vitamin E. Another application of DMQ is to prepare indophenol substituted maltose derivatives, which are used for the determination of the enzymatic activity of α–amylase.

The formation of DMQ appears to proceed in two steps, like steps (1) and (2) in the MD synthesis.

The developed catalytic systems based on HPA-n for catalytic oxidation of phenols and naphthols allow to enhance catalyst selectivity greatly (until 85%) in the both process A and B, to simplify product isolation and catalyst recycling, along with other technological advantages, in compare of the other methods of MD and DMQ synthesis.