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OXIDATION OF 2-METHYLNAPHTHALENE TO 2-METHYL-1,4-NAPHTHOQUINONE WITH HYDROGEN PEROXIDE IN THE PRESENCE OF Pd(II)-POLYSTYRENE SULFONIC ACID RESIN

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The oxidation of 2-methylnaphthalene was carried out in acetic acid with aqueous(60%) hydrogen peroxide in the presence of Pd(II)-polystyrene sulfonic acid resin. 2-Methyl-1,4-naphthoquinone was obtained in a yield of 50 to 60% at 50 °C for 8 h. The catalysts recovered by the filtration were reusable.

2-Methyl-1,4-naphthoquinone(VK_3) and its derivatives have an antihemorrhage activity. As a well known process, 2-methylnaphthalene has been oxidized with a sulfuric acid solution of chromic acid to give the vitamin in 38 to 42% yields.[1) In this process, much efforts are payed for the treatment of waste water. Therefore, some reaction systems using hydrogen peroxide in the presence of acid catalysts have been claimed in patents.[2–4)] Recently, the oxidation has been carried out using ammonium persulfate as an oxidizing agent in the presence of cerium(IV) ammonium sulfate and silver nitrate in an emulsified solution.[5)] However, a more convenient and effective reaction system using solid catalyst has not been proposed yet. We found that Pd(II) acetate fixed on polystyrene sulfonic acid resin effectively catalyzed the oxidation of 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone with aqueous hydrogen peroxide.

The catalysts were prepared from Pd(II) acetate and sulfonic acid polystyrene resin(Dowex 50w, H-form) in acetic acid by stirring for 15 h at room temperature. After the catalyst was washed with the solvent, the oxidation was carried out by the addition of 0.35 g(2.5 mmol) of 2-methylnaphthalene, 0.35 ml(7.8 mmol) H_2O_2 (60%), and acetic acid(10 ml) at 50 °C under magnetic stirring. After almost all H_2O_2 has been consumed(4 h), additional 0.35 ml of H_2O_2 was added and the solution was heated for 4 h to complete the reaction : without divided addition of H_2O_2(60%) the selectivity decreased considerably. The products were analyzed by high-performance liquid chromatography(HPLC) with a M & S Pack(C 18)(4.6 x 150 mm) column using MeOH-H_2O(100 : 15) as an eluent(HPLC conditions: flow rate, 0.5 ml/min; detector, ultraviolet(UV) at 285 nm) and 2,6-dimethylnaphthalene as an internal standard.

Results are shown in Table 1. In the absence of catalysts, the oxidation took place slowly to give 2-methyl-1,4-naphthoquinone in a yield of 7.8% at 50 °C for 8 h. The acid catalyst of polystyrene sulfonic acid resin accelerated the oxidation, but the selectivity to the quinone was poor(28 to 38%) under our reaction conditions. By exchanging a small amount of protons on the resin(one hundredth of its acidity) with palladium(II) ions, the selectivity to 2-methyl-1,4-naphthoquinone was improved from 37.5 to 59.1%. This result suggests that the Pd-exchanged sites on the surface of resin work for the selective oxidation. The conversion also increased with increasing amount of palladium on polystyrene sulfonic acid resin, and reached a maximum value of 90% at 0.24 wt% palladium. At temperatures between 50 to 60 °C, good conversions were obtained with sufficiently high selectivities. After the reaction, the catalyst was separated by filtration. The filtrate was poured into water, and the products were separated as yellow crystals. The catalyst recovered could be reused to give good results (12-1, 12-2).

Table 1. Oxidation of 2-methylnaphthalene with 60% H_2O_2 in the presence of Pd-exchanged polystyrene sulfonic acid resin

Entry No.	Catalyst (g)	Temp °C	Conv. %	Yield %	Select. %
1	No catalyst	50	20.1	7.8	38.5
2	PSx8[a] (1.0)	50	54.9	20.6	37.5
3	PSx12[b] (3.0)	50	64.7	17.8	27.6
4	$Pd(AcO)_2$(0.005)	50	59.1	28.4	48.0
5	0.095%-Pd-PSx8(1.0)	50	82.4	48.7	59.1
6	0.24%-Pd-PSx8(1.0)	50	89.9	50.3	55.9
7	0.24%-Pd-PSx8(1.0)	60	88.8	52.4	59.0
8	0.24%-Pd-PSx8[c] (5.0)	60	88.3	58.7	66.5
9	0.24%-PSx8(1.0)	70	91.7	57.1	62.3
10	0.24%-Pd-PSx12(3.0)	50	93.4	57.5	61.6
11	0.34%-Pd-PSx12(3.0)	50	89.7	59.4	66.2
12-1	0.24%-Pd-PSx8(1.0)	50	97.2	54.2	55.8
12-2		50	96.9	55.2	56.9

2-Methylnaphtharene 0.35 g, 60% H_2O_2 0.7 ml, and AcOH 10 ml were used. a) DOWEX 50W-x8(divinylbenzene 8%, 200-400 mesh, water 50%) and b) DOWEX 50W-x12 (divinylbenzene 12%, 100-200 mesh) were used as supports. c) 2-Methylnaphthalene 1.75 g, 60% H_2O_2 3.5 ml, and AcOH 25 ml were used.

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