Catalytic oxidation of 2-methylnaphthalene and 2-methyl-1-naphthol with 1% Au over hyper crosslinked polystyrene catalyst

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Introduction

Vitamins of K group, or antihemorhagic vitamins, are necessary for a normal fibrillation. It’s applied at strong bleedings, haemorrhagic diathesis and in certain cases of a liver functions frustration. Vitamin K3 (2-methyl-1,4-naphthoquinone, menadione) is a synthetic analog of vitamins of K group.

There are a lot of catalysts described in literature which are applied in the menadione synthesis, however the majority of them gives low selectivity (<40%), is toxic, pollutes the prime product and gives a considerable quantity of by-products [1]. We decided to use the based on HPS catalysts, because of their properties. Hypercrosslinked polystyrene (HPS) is rigid polymeric network of polystyrene linked by methylene bridges. Rigid polymeric matrix of HPS allows stabilizing metal nanoparticles and controlling their growth, due to the presence of nanospores with high degree of monodispersion [2].

At oxidation 2-methylnaphthalene such products, as 2-methyl-1,4-naphthoquinone (menadione, the precursor of vitamin K3), isomerous 6-methyl-1,4-naphthoquinone, methyl groups oxidation products, dinaphthoquinone, epoxiquinone and other products of deep oxidation are formed [1]. 2-methyl-1-naphthol has –OH group and it is made the process of oxidation more selective.

Materials and Methods

At first industrial non-catalytic reaction has been researched. The experiment was conducted as follows: The reactor was charged 20 ml of solvent, 0.1 g of 2-methylnaphthalene or 2-methyl-1-naphthol. The reactor was thermostated to the necessary temperature (70-100°C). Every 15 minutes 1 ml of 30%H2O2 were added in the solution. The oxidation was performed 4-5 hours. In the experiment, every 15 minutes samples were taken and analysed by gas chromatography GC-MS on «Shimadzu-2010 MS». The catalytic experiment was conducted as non-catalytic, and 0.05 g of 1% Au/MN270 (hyper crosslinked polystyrene) was added. HPS were obtained from Purolite Inc. 1% Au/MN270 catalyst was prepared as follows: 3 g of polymer impregnated 0.0623 g HAuCl4•2H2O in 8.5 ml of THF (tetrahydrofurran) at field capacity. Dried at 70°C. Next treated Na2CO3 0.2 g in 12 ml H2O. Conduct a second drying. Then washed to a pH of 7.1.

Results and Discussion

Processes with 2-methylnaphthalene were carried out in acetic acid, because the conversion in other solvent were negligible. It can be explained by the formation of peracetic acid, which oxidize the substrate.

In the case of non-catalytic oxidation process the maximum selectivity is reached at 90°C at 80% of conversion. The menadione yield is 40% for 2-methylnaphthalene. And for 2-methyl-1-napthol the menadione yield is 53%.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Selectivity, %</th>
<th>Conversion, %</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methylnaphthalene</td>
<td>50</td>
<td>80</td>
<td>40</td>
</tr>
<tr>
<td>2-methyl-1-naphthol</td>
<td>96</td>
<td>55</td>
<td>55</td>
</tr>
</tbody>
</table>

Catalytic oxidation process. The menadione yield for 2-methylnaphthalene makes 58% for 2-methylnaphthalene. And for 2-methyl-1-napthol the menadione yield makes 73%.

<table>
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</tr>
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<tbody>
<tr>
<td>2-methylnaphthalene</td>
<td>64</td>
<td>90</td>
<td>58</td>
</tr>
<tr>
<td>2-methyl-1-naphthol</td>
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Acknowledgements

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References