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Oxidation of hydroquinones to benzoquinones with hydrogen peroxide using catalytic amount of silver oxide under batch and continuous-flow conditions

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ABSTRACT

Silver oxide (Ag_2O) can be utilized as heterogeneous catalyst in the oxidation of hydroquinones to the corresponding benzoquinones with 30% aq. H_2O_2. The catalytic properties of Ag_2O have been explored in the model reaction of methylhydroquinone with H_2O_2 performed under batch conditions. Results show that the reaction can be carried out in high yield and selectivity at room temperature under environmentally friendly conditions. The truly heterogeneous catalyst can be recovered by filtration and reused for at least five times, giving the same excellent results (~95% yield, ~98% selectivity). The catalyst can be packed in a tubular reactor and utilized under continuous-flow conditions giving similar good results.

1. Introduction

Quinones [1] and the parent *p*-quinols [2] are found as structural units in a great variety of bioactive natural compounds showing antifungal, antibacterial, antiviral, antigerminative, and anticancer activities. They are consequently useful intermediates for organic synthesis with particular interest into the production of biologically active compounds [3]. For example, trimethyl-1,4-benzoquinone is a key reagent in the synthesis of vitamin E and 2-methyl-1,4-naphthoquinone (vitamin K3), an important additive in animal feed, is also utilized for construction of vitamin K1 [4].

The most general method to obtain quinones is the oxidation of monohydroxyaromatics and dihydroxyaromatics. The oxidation of substituted hydroquinones to the corresponding quinones has been achieved by a variety of oxidants [5]. For example, the Fremy's salt (potassium nitrodisulfonate) [5a,b], sodium dichromate/sulfuric acid mixture [5c,d], benzyltrimethyl-ammonium tribromide [5e], iodine or hydroiodic acid/hydrogen peroxide mixture [5f], diphenyl diselenide/hydrogen peroxide mixture [5g], *tert*-butyl hydroperoxide/ceric ammonium nitrate mixture [5h], phenyl iodosoacetate on alumina under microwave irradiation [5i], and different transition metal salt derivatives [5j] have been exploited, but most of these reagents suffer from the drawback of producing large amounts of noxious waste.

Phenols and naphthols could be directly converted into quinones via one-pot hydroxylation–oxidation process in the presence of different oxidizing agents such as ammonium persulfate on wet silica [6], hydrogen peroxide–methyltrioxorhenium in ionic liquids [7]. The dye-sensitized photooxygenation of 1,5-dihydroxynaphthalene to Juglone with oxygen in the presence of moderately concentrated sunlight (and solid-supported sensitizers) represents an interesting example of environmentally friendly alternative to common thermal processes [8].

The use of immobilized catalysts for selective oxidation in liquid phase represents a great synthetic improvement [9]. As an example, hydroquinone was efficiently oxidized to *p*-benzoquinone with hydrogen peroxide in the presence of acrylic resin-supported Cu(II) catalyst [10]. Moreover, phenols containing oxidizable groups could be directly and selectively oxidized to *p*-benzoquinones with hydrogen peroxide using a mesoporous titanium silicate catalyst [11]. Furthermore, a catalyst based on platinum nanoclusters incarcerated into a styrene polymer was, more recently, reported for the aerobic oxidation of hydroquinones to quinones [12].

Well-known and established reagents such as silver oxide and silver carbonate show synthetic utility at the laboratory level for these oxidative reactions [3a,13] but they are evidently not practical for large-scale preparation due to their high cost.

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New green legislations call for the lowering of waste production and use of more friendly alternative reagents and catalysts. This goal can be achieved through the application of the principles of green chemistry that provide a framework for designing more eco-compatible routes to fine chemical production [14]. According to this strategy, herein we wish to report results of a study concerning the use of silver(I) oxide as solid catalyst in the oxidation of hydroquinones to quinones by hydrogen peroxide [15] at room temperature under batch and continuous-flow conditions. To our knowledge, silver(I) oxide has been previously utilized only as reagent in stoichiometric amount in the same reaction [3a,13].

2. Experimental

2.1. Materials

All catalysts, namely Ag, Ag_2O, V_2O_5, CrO_2 (Magtrieve™), TiO_2, MoO_3, $AgNO_3$, and solvents were purchased from Aldrich and were used without previous purification, except for MeOH which was distilled before use. Hydrogen peroxide 30 wt.% in H_2O was also purchased from Aldrich and was used from freshly opened containers. The following reagents were utilized without further purification: hydroquinone $\geqslant$99% (Aldrich), methylhydroquinone 99% (Aldrich), methoxyhydroquinone 98% (Aldrich), 1,4-dihydroxy-2,6-dimethoxybenzene 97% (Aldrich), 1,4-dihydroxynaphthalene $\geqslant$90% (Aldrich), chlorohydroquinone ~85% (Fluka). Isopentenyl hydroquinone was synthesized as reported in the literature [16].

Elemental analyses were performed with a Carlo Erba CHNS-O EA1108 Elemental Analyzer.

The purity of commercially available hydroquinones was carefully controlled by GC or HPLC analyses due to their well-known instability during time.

Conversions and yields were determined by GC analysis, performed on a TraceGC ThermoFinnigan instrument (fused silica capillary column SPB-20 from Supelco (30 m × 0.25 mm) was used with helium as carrier) adding 1,4-dimethoxybenzene as internal standard.

2.2. Catalytic testing

As examples, we report here the optimized methods. The catalytic tests have been performed by similar procedures with the amounts of reagents reported in the notes of tables and figures.

2.2.1. Typical procedure: oxidation of methylhydroquinone (batch experiment)

To a mixture of methylhydroquinone (0.12 g, 1 mmol), Ag_2O (0.02 g, 0.1 mmol), and MeOH (2 mL), stirred for 5 min, a solution of 30% aq. H_2O_2 (0.24 mL, 2.4 mmol) in MeOH (10 mL) was added dropwise under stirring in 10 min at room temperature. Then, the mixture was continuously stirred for 20 min at room temperature. Subsequently, the reaction mixture was diluted with water (10 mL) and then extracted with diethyl ether (2 × 15 mL). The combined organic layers were washed with water (2 × 10 mL) and dried over Na_2SO_4. The solvents were evaporated under reduced pressure affording product **3a** (0.11 g, 92% yield).

2.2.2. Typical procedure: oxidation of methylhydroquinone (continuous-flow experiment)

Silica-KG-60 (Merck) for column chromatography sieved to 80 mesh (1.85 g) and Ag_2O (0.093 g) without any previous treatment were mixed and packed with methanol in a column reactor (10 cm length, 0.8 cm inner diameter) equipped with a syringe pump. Methanol was passed at room temperature for 15 min to achieve column reactor conditioning with a 0.7 mL/min flow rate. The solution of premixed reagents methylhydroquinone (4.5 g, 36 mmol) and 30% aq. H_2O_2 (8.65 mL, 86.4 mmol) in methanol (50 mL) was passed at room temperature with the same flow rate (0.7 mL/min) with a modest pressure (~0.2 bar); the time for passage of the entire solution was about 85 min. The column reactor was finally rinsed by passing methanol (20 mL) and the eluates were combined. After removal of methanol and filtration to remove traces of silica, the product **3a** was crystallized by toluene/hexane mixture (4.12 g, 94% yield).

The products prepared by both methods were sufficiently pure (>97%) for possible synthetic use. For analytical purposes, they were further purified by flash chromatography over silica gel columns with hexane/ethyl acetate mixtures as eluent.

3a. Anal. Calcd for $C_7H_6O_2$: C, 68.85, H, 4.95. Found: C, 68.98, H, 4.80; mp. 70 °C (Lit. [17] 69 °C).
3b. Anal. Calcd for $C_6H_4O_2$: C, 66.67, H, 3.73. Found: C, 66.50, H, 3.82; mp. 113–115 °C (Lit. [18] 112–114 °C).
3c. Anal. Calcd for $C_7H_6O_3$: C, 60.87, H, 4.38. Found: C, 60.95, H, 4.45; mp. 144–146 °C (Lit. [19] 145–146 °C).
3d. Anal. Calcd for $C_6H_3ClO_2$: C, 50.56, H, 2.12. Found: C, 50.72, H, 2.30; mp. 53–56 °C (Lit. [17] 55–56 °C).
3e. Anal. Calcd for $C_9H_{10}O_2$: C, 71.98, H, 6.71. Found: C, 72.10, H, 6.78; mp. 31–33 °C (Lit. [18] 31–32 °C).
3f. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98, H, 6.86. Found: C, 74.90, H, 6.77; mp. 100–103 °C (Lit. [20] 102 °C).
3g. Anal. Calcd for $C_8H_8O_4$: C, 57.14, H, 4.80. Found: C, 57.01, H, 4.76; mp. 255–258 °C (Lit. [21] 254–256 °C).
3h. Anal. Calcd for $C_{10}H_6O_2$: C, 75.94, H, 3.82. Found: C, 75.81, H, 3.72; mp. 120–122 °C (Lit. [17] 121–122 °C).

3. Results and discussion

Our experiments to achieve the optimum reaction conditions began with the oxidation of methylhydroquinone **1a** selected as model reagent (1 mmol) with 30% aq. H_2O_2 **2** (2 mmol) catalyzed by some classic, commercially available oxidation catalysts (0.1 mmol). The experiments were carried out at room temperature in methanol, acetone, water or their mixtures, and 30% aq. H_2O_2 diluted in the selected solvent was added dropwise during 10 min. The reaction mixture was stirred for further 20 min at room temperature.

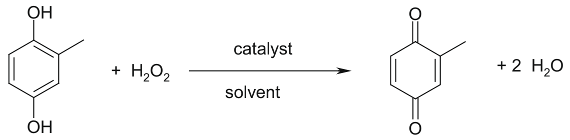
Table 1 shows the yields and selectivities for all catalysts and solvents.

To our pleasure, some of the tested metal oxides showed satisfactory catalytic activity giving product **3a** in good yields: V_2O_5, MoO_3, and Ag_2O afforded **3a** in 82%, 78%, and 84% yield, respectively (Table 1, entries 2, 5, and 6).

The best selectivity with respect **3a** (99%) was achieved with Ag_2O (Table 1, entry 6), whereas with V_2O_5 and MoO_3, the selectivity was lower due to the competitive production of substituted biaryls (~8–10%) via oxidative homocoupling of **1a** (Table 1, entries 2 and 5). Silver nitrate was less active than silver(I) oxide (Table 1, entry 7). Results from Table 1 also suggest that methanol was the solvent of choice in terms of yield, selectivity, and solubility of both starting materials and products (Table 1, entry 6). Use of different polar solvents resulted in comparable high yield but lower selectivity (Table 1, entries 8 and 11).

Parallel leaching studies were carried out by catalyst filtration at 25 °C after 10 min reaction time when the yield of **3a** was 55% [22]. No yield increase was observed by keeping the filtrate at 25 °C for further 20 min when Ag_2O was utilized as catalyst. On the contrary, amounts of active species were leached into solution when the reaction was performed in the presence of V_2O_5 and

Table 1
Reaction of methylhydroquinone (**1a**) with aq. H_2O_2 (**2**) in the presence of different solid catalysts and solvents.[a]



1a **2** **3a**

No.	Catalyst	Solvent	**3a** yield (select.)[b] (%)
1	–	MeOH	~3
2	V_2O_5	MeOH	82 (88)
3	CrO_2 (Magtrieve)	MeOH	38 (95)
4	TiO_2	MeOH	15 (99)
5	MoO_3	MeOH	78 (90)
6	Ag_2O	MeOH	84 (99)
7	$AgNO_3$	MeOH/H_2O 20/80	30 (75)
8	Ag_2O	Acetone	80 (95)
9	Ag_2O	H_2O	82 (99)
10	Ag_2O	MeOH/H_2O 50/50	82 (99)
11	Ag_2O	MeCN	92 (92)

[a] Catalyst 0.1 mmol, methylhydroquinone (**1a**) 1 mmol, solvent 2 mL, 30% aq. H_2O_2 2 mmol in solvent 10 mL, reaction temperature 25 °C, reaction time 10 min addition and 20 min reaction.

[b] Determined by GC analysis.

MoO_3. For this reason, Ag_2O was utilized as truly heterogeneous catalyst in successive studies.

The effect of catalyst amount (expressed as Ag_2O/**1a** molar ratio) was then evaluated in the model reaction of Table 1 while keeping the molar ratio of **1a**:**2** at 1:2, room temperature, reaction time 10 + 20 min and methanol as solvent. The yield and selectivity of product **3a** are plotted against the amount of catalyst in Fig. 1.

In the absence of Ag_2O, product **3a** was obtained in traces (~3%). However, the **3a** yield was dramatically increased to 71% when only 0.05 molar ratio Ag_2O/**1a** was utilized. The maximum performance was achieved when the Ag_2O/**1a** molar ratio was 0.1, being product **3a** obtained in 86% yield. By further increasing Ag_2O/**1a** molar ratio, the yield and, in particular, the selectivity of product **3a** underwent a little, but continuous lowering. This is due to the special oxidizing property of Ag_2O that is known to give competitive oxidative coupling of phenols including hydroquinones [3].

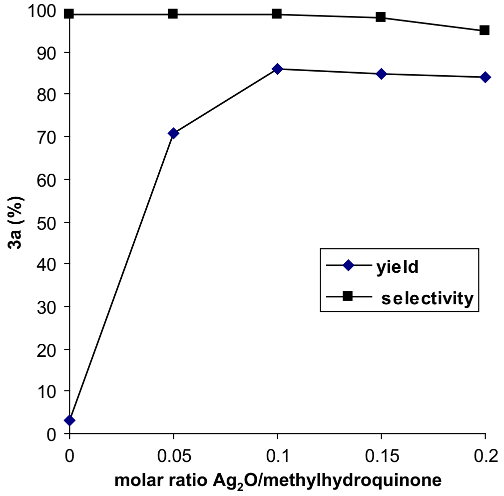


Fig. 1. Effect of the amount of catalyst (Ag_2O) on the product **3a** yield and selectivity. Reaction conditions: methylhydroquinone (**1a**) 1 mmol, MeOH 2 mL, 30% aq. H_2O_2 2 mmol in MeOH 10 mL, reaction temperature 25 °C, reaction time: 10 min addition and 20 min reaction.

With the goal of achieving the optimum efficiency, the effect of the amount of H_2O_2 on the yield of product **3a** was also explored. To this end, yield and selectivity of product **3a** were determined in the model reaction performed in methanol, at room temperature, for 10 + 20 min in the presence of 10% mol of Ag_2O and with increasing amounts of 30% aqueous H_2O_2.

Results reported in Fig. 2 confirm that Ag_2O alone converts methylhydroquinone **1a** into the product **3a** without addition of hydrogen peroxide. However, product **3a** was obtained in 20% yield instead of the expected 10% based on the stoichiometry of the reaction. The higher yield was attributed to the presence of atmospheric oxygen that could be involved in the oxidative process. Indeed, by performing the reaction under nitrogen atmosphere in a degassed solvent, product **3a** was obtained in 8% yield [23]. These results represent a quite interesting example of green oxidation process that is under investigation in our group.

Fig. 2 also shows that the increase of the H_2O_2 amount (from 0 to 2.5 H_2O_2/**1a** molar ratio) gave a linear increase of the yield of product **3a** from 20% to 96%. The selectivity was constant around 98%; and only when larger amounts of H_2O_2 were utilized, the selectivity decreased due to the mentioned overoxidative processes.

Concerning the catalyst recycling, we have observed that in the model reaction of Table 1, the catalyst Ag_2O, simply recovered by filtration, washed with hot methanol could be reused at least five times, without further activation, giving product **3a** with unchanged high yield and selectivity (Fig. 3).

The sole drawback we observed was the increasing crumbling of the catalyst particles due to the mechanical stress produced by stirring that made more difficult the catalyst recovery by filtration.

The scope and generality of this process with respect to various hydroquinones is illustrated in Table 2.

A variety of functionalized quinones could be prepared in good yield and excellent selectivity. The reaction tolerated both electronwithdrawing and electrondonating groups (Table 2, entries 3 and 4).

Due to the mild oxidizing conditions, 1,4-dihydroxy-2-(3′-methylbut-2′-enyl)benzene can be efficiently converted into the corresponding quinone without over-oxidation or epoxide production also after prolonged reaction time (Table 2, entry 6) [24]. In some cases, the reaction required longer reaction times (Table 2, entries 2, 3, 4 and 7).

The good synthetic results and, in particular, the effective catalyst recyclability achieved in the batch experiments prompted us to develop a reaction method based on a continuous-flow catalytic

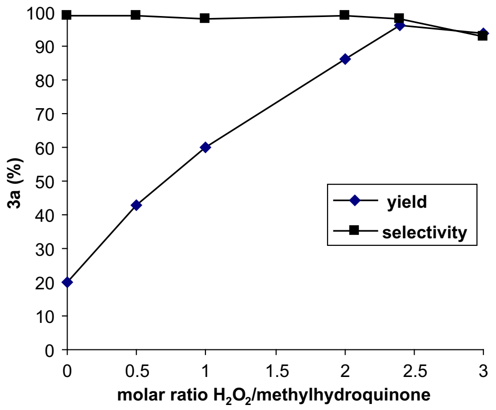


Fig. 2. Effect of molar ratio H_2O_2/methylhydroquinone on the product **3a** yield and selectivity. Reaction conditions: Ag_2O 0.1 mmol, methylhydroquinone (**1a**) 1 mmol, MeOH 2 mL, reaction temperature 25 °C, reaction time: 10 min addition and 20 min reaction.

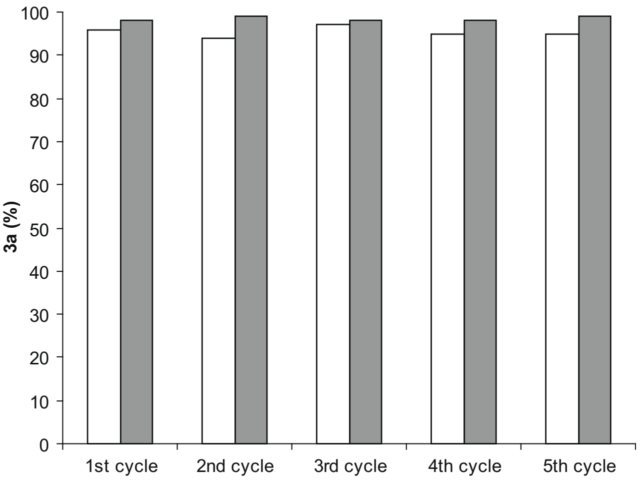
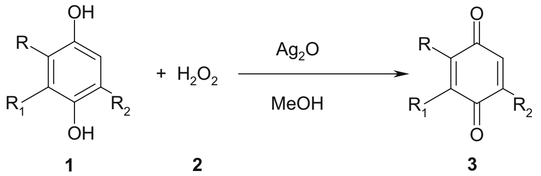


Fig. 3. Relative activity of Ag_2O in five successive cycles of the model reaction after washing with hot methanol (☐ yield of **3a**; ■ selectivity of **3a**).

Table 2
Reaction of various hydroquinones (**1**) with aq. H_2O_2 (**2**).[a]



No.	R	R_1	R_2	3	Time (min)	**3** yield (select.)[b] (%)
1	Me	H	H	**3a**	20	96 (98)
2	H	H	H	**3b**	40	94 (99)
3	OMe	H	H	**3c**	40	70 (95)
4	Cl	H	H	**3d**	40	90 (97)
5	Me	Me	Me	**3e**	20	92 (98)
6	$CH_2CH{=}CMe_2$	H	H	**3f**	20	98 (98)
7	H	OMe	OMe	**3g**	40	97 (98)
8	CH=CH–CH=CH		H	**3h**	20	99 (97)

[a] Ag_2O 0.1 mmol, hydroquinone (**1**) 1 mmol, MeOH 2 mL, 30% aq. H_2O_2 2.4 mmol in MeOH 10 mL, reaction temperature 25 °C, reaction time 10 min addition and 20 (or 40) min reaction.

[b] Determined by GC analysis.

system for performing the model reaction. Such a system, once optimized, can allow for a rapid, easy, and efficient synthesis and purification of the target compounds [25]. Indeed, the continuous-flow process is, in short, an integrated reaction and separation approach that can be regarded as one of the most efficient contributions to the process intensification [26].

To this end, a simple apparatus was constructed using a standard laboratory small chromatographic column (10 cm length × 0.8 cm inner diameter) packed with a mixture of Ag_2O (0.093 g) and KG-60 silica for column chromatography (1.85 g) sieved to 80 mesh and equipped with a syringe pump to charge the reaction mixture and to carefully control the flow rate. The column reactor was previously washed by flowing MeOH (10 mL) for 15 min at 0.7 mL/min flow rate at room temperature; then, a solution of methylhydroquinone **1a** (36 mmol) and 30% aq. H_2O_2 (86.4 mmol) in MeOH (50 mL) was passed at room temperature with the same flow rate (0.7 mL/min) and a minimum pressure applied (~0.2 bar). The column reactor was then rinsed with additional MeOH (10 mL), and the combined eluates were analyzed by GC giving product **3a** in 98% yield.

To evaluate the stability and efficiency during time of the column reactor, the same experiment was repeated six times at one-day intervals giving product **3a** with the following yields: 1st 98%, 2nd 97%, 3rd 98%, 4th 99%, 5th 96%, and 6th 98%. Given the effectiveness of the present column reactor and experimental ease of its assembling and use in the oxidation of hydroquinones to quinones, such system could hold promise for the future larger-scale application.

We have not investigated the reaction mechanism; however, the experimental results achieved in this study may allow us to make some general mechanistic comments. It is well known that different metals may catalyze oxidation of phenolic compounds affording numerous products by a variety of ways. The mechanistic rationalizations of these reactions are frequently difficult and give conflicting results even in reactions performed under homogeneous conditions. We have initially assumed, for the Ag_2O/H_2O_2 combination, a pathway similar to that for $Cu(I)/H_2O_2$ system involving generation of hydroxyl radicals [27]. However, when the model reaction was performed in the presence of a stoichiometric amount of the radical scavenger 2,6-di-*tert*-butyl-4-methylphenol with respect reagent **1a**, product **3a** was obtained in 86% yield showing only a modest deactivation. In addition, no paramagnetic species could be recognized by a preliminary EPR analysis of the reaction mixture.

These results seem to be in better agreement with a heterolytic catalysis process where free radicals are not crucial intermediates. Furthermore, all critical steps of the entire oxidative reaction seem to occur on the surface of the catalyst and no active species are leached into solution. This is confirmed by both the filtration test already described in this study [22] and the "pre exposure" test recommended by Jacobs and coworkers [28] that confirmed the great stability of Ag_2O under the reaction conditions and further demonstrates that every key species is produced and reacts on the surface of the catalyst. Quite interesting on this subject are results achieved by performing the model reaction under homogeneous conditions (Table 1, entry 7). Indeed, the reaction performed in the presence of $AgNO_3$ in water–methanol mixture as solvent gave lower conversion of reagent **1a** and modest selectivity, being product **3a** accompanied by different amounts of C—C and C—O linked biaryl by-products due to the competitive oxidative coupling of the hydroquinone [29].

A possible essential catalytic cycle is described in Fig. 4 on the basis of experimental and literature information. It is, indeed, known from literature and confirmed in this study that Ag_2O oxidizes hydroquinones to benzoquinones in stoichiometric ratio being reduced to metal silver that can be reoxidized to Ag_2O and other silver oxides by H_2O_2 as very early reported in the literature [30]. Furthermore, in the blank experiment, we observed that the commercially available silver powder (<250 μm, 99.99%) gives product **3a** in 25% yield when utilized as catalyst in the model

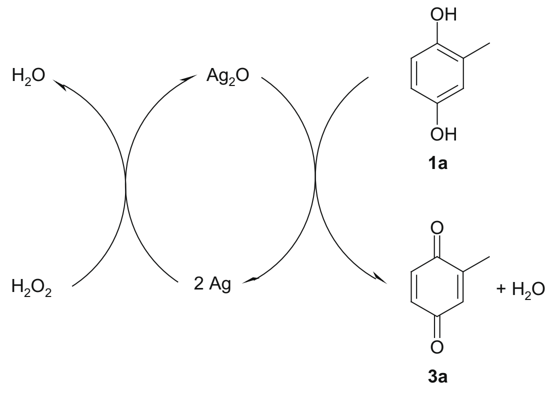


Fig. 4. Proposed general mechanism.

reaction. Finally, the possible intervention of the alcoholic solvent MeOH as a reagent able to give the corresponding hydroperoxide intermediate by primary reaction with H_2O_2 [31] cannot be excluded even if product **3a** has been also obtained in 90% yield by performing the model reaction in acetonitrile.

4. Conclusion

We have demonstrated that the commercially available silver oxide (Ag_2O), until now utilized as reagent in stoichiometric amount to perform oxidation of hydroquinones to quinones, can be now exploited as efficient heterogeneous catalyst in the same reaction with 30% aqueous H_2O_2. The catalytic properties of Ag_2O in the model reaction of methylhydroquinone with H_2O_2 have been explored. The results show that the reaction can be performed in high yield and selectivity at room temperature under environmentally friendly operating conditions. The truly heterogeneous catalyst can be recovered by filtration and reused for, at least, five times giving the same excellent results.

The catalyst can be dispersed in silica and packed in a tubular reactor that can be more efficiently utilized to perform the same oxidation reaction under continuous-flow conditions with a minimum pressure applied. The column reactor can be utilized at least six times during one week without any lowering of activity.

The catalyst is very active and selective for the oxidation of a series of hydroquinones to the corresponding quinones; and due to its soft oxidizing properties, it can be efficiently utilized also with compounds containing oxygen sensitive groups.

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