

Article

Highly Active Trifloaluminate Ionic Liquids as Recyclable Catalysts for Green Oxidation of 2,3,6-Trimethylphenol to Trimethyl-1,4-Benzoquinone

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Abstract: An effective method for the synthesis of 2,3,6-trimethyl-1,4-benzoquinone via the oxidation of 2,3,6-trimethylphenol as the key step in the in the preparation of vitamin E was presented. An aqueous solution of H₂O₂ was used as the oxidant and Lewis acidic trifloaluminate ionic liquids [emim][OTf]-Al(OTf)₃, $\chi_{\text{Al(OTf)}_3}$ = 0.25 or 0.15 as catalysts. Trifloaluminate ionic liquids were synthesised by the simple reaction between 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (triflate) [emim][OTf] and aluminium triflate used in sub-stoichiometric quantities. The influence of the reaction parameters on the reaction course, such as the amount and concentration of the oxidant, the amount of catalyst, the amount and the type of organic solvent, temperature, and the reaction time was investigated. Finally, 2,3,6-trimethyl-1,4-benzoquinone was obtained in high selectivity (99%) and high 2,3,6-trimethylphenol conversion (84%) at 70 °C after 2 h of oxidation using a 4-fold excess of 60% aqueous H₂O₂ and acetic acid as the solvent. The catalytic performance of trifloaluminate ionic liquids supported on multiwalled carbon nanotubes (loading of active phase: 9.1 wt.%) was also demonstrated. The heterogeneous ionic liquids not only retained their activity compared to the homogenous counterparts, but also proved to be a highly recyclable catalysts.

Keywords: ionic liquids; supported ionic liquid phase; carbon nanotubes; trifloaluminate ionic liquids; Lewis acids; oxidation of 2,3,6-trimethylphenol; 2,3,6-trimethylhydroquinone

1. Introduction

Functionalised benzoquinones are attractive building blocks for a wide range of bioactive compounds, fine chemicals, and pharmaceuticals [1,2]. Trimethyl-1,4-benzoquinone (TMBQ), obtained by the oxidation of 2,3,6-trimethylphenol (TMP), is an intermediate in the synthesis of vitamin E, the most important biological antioxidant soluble in lipids (Figure 1) [3]. As the first stage of this synthesis, the oxidation of TMP to TMBQ (Figure 1a) takes place. In the next step, the hydrogenation of TMBQ to 2,3,6-trimethylhydroquinone (Figure 1b) proceeds with the subsequent cycloaddition of 2,3,6-trimethylhydroquinone to isophytol leading to the formation of vitamin E (Figure 1c) [4].

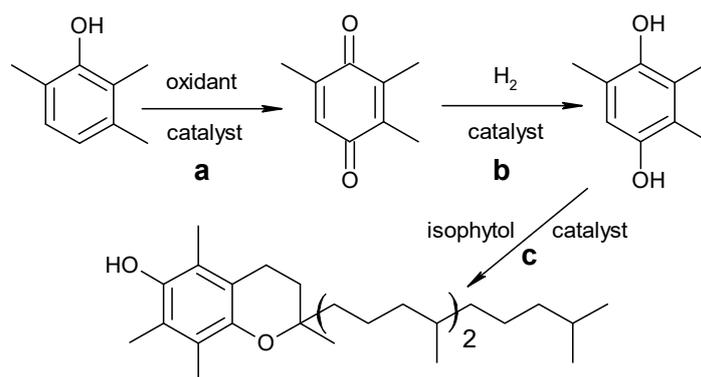


Figure 1. Three-step synthesis of vitamin E: (a) oxidation of 2,3,6-trimethylphenol; (b) hydrogenation of 2,3,6-trimethyl-1,4-benzoquinone; and (c) cycloaddition of 2,3,6-trimethylhydroquinone to isophytol [5].

The constantly growing number of environmental regulations have forced the development of sustainable catalytic methods for the oxidation processes. For ecological and economic reasons, the use of inexpensive and commercially available oxidants together with an active catalyst is crucial for the synthesis of the key intermediate TMP. The current industrial method for the production of TMP is the oxidation of TMBQ with oxygen using copper chloride in stoichiometric amounts [5,6]. As a result of the presence of a chlorine atom in the catalyst molecule, chlorinated by-products are formed. This issue generates problems with corrosion. To tackle this problem, to reduce the metal chloride to catalytic amounts, ionic liquid 1-butyl-3-methylimidazolium chloride and *n*-butanol as a co-solvent were used, affording a 86% yield of TMP [7]. Another approach is to use copper(II) nitrate catalyst in water generating halogen-free conditions [8].

Simultaneously, the studies on the active catalysts for the oxidation of TMP with the use of H₂O₂ as a green oxidant were carried out. However, due to the fact that hydrogen peroxide is a weak oxidant, the water-stable catalysts which can activate H₂O₂ are still in demand. According to this trend, the use of heteropolyacid catalyst allowed to obtain TMBQ in an 85% yield, after 4 h at 70 °C, using a 60% aqueous solution of H₂O₂ [9]. The use of a more concentrated 83% solution of H₂O₂ with methyltrioxorhenium(VII) as a catalyst and acetic acid in the oxidation of TMP yielded in 70% of TMBQ after 2 h at 60 °C [10]. The ruthenium compounds were also used as a catalyst for this process. Under the optimised conditions (30% aqueous solution of H₂O₂, acetic acid as a solvent, 2 h at 80 °C), TMBQ was obtained with 89% of yield [11]. The use of iron(III) compounds as catalysts allowed to achieve a high yield of TMBQ (79%) after 2 h at 80 °C [12]. In all cases, practically 100% conversion of the substrate was achieved, nevertheless, the lower yields were caused by the presence of oxidation side-products.

A series of heterogeneous silica-supported titania, Ti- and V-containing mesoporous mesophase catalysts as well as Ti-monosubstituted polyoxometalate catalysts, were developed by Kholdeeva's group [13–18]. To date, the most active catalyst for the oxidation of TMP with hydrogen peroxide is a heteropolyacid with vanadium and tungsten atoms in its structure, based on the tetra *n*-butylammonium cation TBA₄H[γ-PW₁₀V₂O₄₀]. The use of a 35% aqueous solution of H₂O₂ and acetonitrile as a solvent led to a 99% conversion of TMP with 99% selectivity to TMBQ after only 5 min at 80 °C [18].

Searching for halogen-free and water-stable Lewis acidic catalysts for organic synthesis, in our previous work, new acidic trifluoroaluminate ionic liquids were presented [19,20]. Trifluoroaluminate ionic liquids were synthesised in analogy to chlorometallate systems [21] with the difference that instead of the chlorido ligands on Al atoms, trifluoromethanesulfonate (triflate, OTf) ligands were present. The synthesis is the simple reaction between triflate ionic liquids [cation][OTf] (1-alkyl-3-methylimidazolium cation—[emim]⁺ and [omim]⁺) and aluminium triflate used in sub-stoichiometric quantities (molar ratio Al(OTf)₃: χ_{Al(OTf)₃} = 0.15 and 0.25). As a result, viscous ionic liquids with higher melting points than the chloroaluminate counterparts and lower acidity

(Acceptor Number AN = ca. 68 versus 96), however, with higher stability towards hydrolysis in the presence of atmospheric moisture, were obtained. The oligonuclear anionic complexes having various triflate bridging modes were postulated to create anions. The catalytic performance of these systems as acidic catalysts was presented in the synthesis of chromanes [19] and alkyl levulinates [20].

In this work, the use of trifloaluminate ionic liquids as catalysts in the homogenous oxidation of TMP with an aqueous solution of H_2O_2 to TMBQ was proposed. To facilitate the catalyst separation and its recycling, the ionic liquid was also immobilised on multiwalled carbon nanotubes (MWCNTs), presenting the superactive, selective and stable heterogeneous catalyst crucial for the development of sustainable synthetic processes.

2. Results and Discussion

Trifloaluminate ionic liquids based on 1-ethyl-3-methylimidazolium cation $[emim]^+$ with various molar ratio of $Al(OTf)_3$ to $[emim][OTf]$: $\chi_{Al(OTf)_3} = 0.25$; $\chi_{Al(OTf)_3} = 0.15$ were selected as the Lewis acidic catalysts (Figure 2). The synthesis was performed in the glove-box to avoid the hydrolysis under the solventless conditions. Ionic liquids were obtained in 99% yield as yellow liquids and characterised using the NMR spectroscopy for the estimation of activity coefficients of the target components (NEAT-NMR).

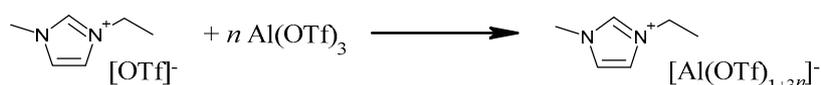


Figure 2. The synthesis of ionic liquids.

The obtained ionic liquids were used for the oxidation of TMP with an aqueous solution of H_2O_2 (Figure 3). It is worth underlining that the crucial factor in oxidation is selectivity. During the oxidation of TMP to TMBQ, the following side-products can be formed (Figure 3): 2,2',3,3',5,5'-hexamethyl-4,4'-biphenol (BP), 2,3,6-trimethyl-1,4-benzoquinone epoxides (EQ) and 2-hydroxy-3,5,6-trimethyl-1,4-benzoquinone (HO-TMBQ).

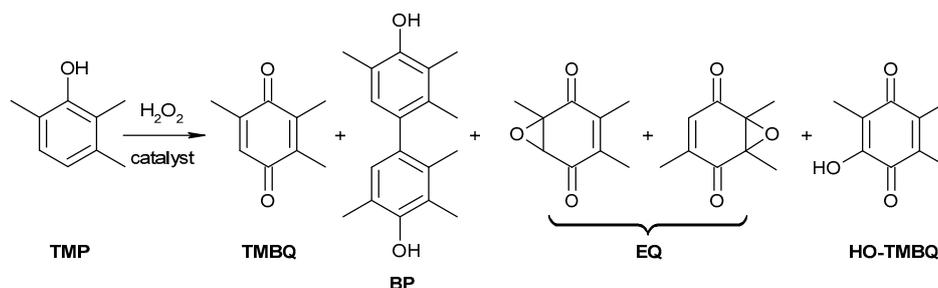


Figure 3. Oxidation of 2,3,6-trimethylphenol (TMP) to 2,3,6-trimethyl-1,4-benzoquinone (TMBQ) and potential by-products.

2.1. Homogeneous System with Trifloaluminate Ionic Liquids

The preliminary tests were carried out using a 4-fold molar excess of 60% aqueous solution of H_2O_2 in relation to TMP in solventless conditions at 70 °C (Table 1).

Table 1. The influence of the structure and amount of trifluoroaluminate ILs (ionic liquids) on the course of the oxidation of TMP to TMBQ under solventless conditions. Reaction conditions: TMP (5 mmol), 60% aq. H₂O₂ (20 mmol), 70 °C, 2 h.

Entry	IL	mol% of IL ¹	TMP Conversion (%)	TMBQ Selectivity (%)
1	[emim][OTf]-Al(OTf) ₃ , χ _{Al(OTf)₃} = 0.15	3	41	73
2	[emim][OTf]-Al(OTf) ₃ , χ _{Al(OTf)₃} = 0.25	3	77	79
3	[emim][OTf]-Al(OTf) ₃ , χ _{Al(OTf)₃} = 0.25	2	83	72

¹ with respect to TMP, conversion and selectivity were measured using GC.

In the absence of solvent, [emim][OTf]-Al(OTf)₃, χ_{Al(OTf)₃} = 0.15 showed very low catalytic activity, resulting in 41% TMP conversion and 73% selectivity to TMBQ (entry 1, Table 1). The use of [emim][OTf]-Al(OTf)₃, χ_{Al(OTf)₃} = 0.25 allowed to obtain higher conversion and selectivity values, i.e., 77 and 79%, respectively. As the amount of ionic liquid increased, the selectivity to TMBQ increased while the TMP conversion decreased. This is due to the formation of two phases during the reaction. At the start of the reaction, all the reagents and the catalyst were dissolved, but, after the reaction, the product along with the occluded side-products and the unreacted substrate precipitated as a red solid. Therefore, to improve the catalytic efficiency of the process, the addition of a solvent was used (Table 2).

Table 2. The influence of the solvent on the course of the oxidation of TMP to TMBQ. Reaction conditions: TMP (5 mmol), 60% aq. H₂O₂ (20 mmol), [emim][OTf]-Al(OTf)₃, χ_{Al(OTf)₃} = 0.25 (2 mol%), solvent (3 cm³), 70 °C, 2 h.

Entry	Solvent	TMP Conversion (%)	TMBQ Selectivity (%)
1	CH ₃ COOH	88	92
2 ¹	CH ₃ COOH	31	89
3 ²	CH ₃ COOH	79	79
4	CH ₃ COOH + CH ₃ CN	69	80
5	CH ₃ CN	6	86
6	<i>n</i> -BuOH	10	73
7	MeOH	9	71

¹ without IL; ² [emim][OTf]-Al(OTf)₃, χ_{Al(OTf)₃} = 0.25 (0.1 mol%), conversion and selectivity were measured using GC.

The use of polar solvents (CH₃CN, *n*-BuOH and MeOH) resulted in a lower reaction rate and a decrease in TMP conversion due to the dilution of the reaction system. On the other hand, the addition of acetic acid caused the increase in the catalytic activity (up to 88% conversion and up to 92% selectivity). Acetic acid emerged as the essential reagent in this free radical oxidation. It is known that it increases the speed of the termination step in the formation of the final product and reduces the contribution of the propagation step. Such a combination of events, in total, decreases the amount of side-products [22]. The use of acetic acid alone without the ionic liquid also allowed to obtain the product with high selectivity (89%), however, the TMP conversion was poor (31%). The lowering of the amount of IL did not cause a significant decrease in catalytic activity (entry 3, Table 2).

The amount of solvent and the duration of the process significantly influenced the reaction course (Table 3). The addition of 1 mL of acetic acid provided homogeneous conditions and using only 0.1 mol% of IL led to a 77% conversion of TMP to TMBQ with 78% selectivity, after only 2 h. Extending the reaction time to 4 h allowed to achieve 84% selectivity with the nearly full conversion of TMP. Increasing the temperature to 100 °C increased the reaction rate resulting in 99% TMP conversion

just after 2 h and 86% selectivity of product. However, due to the safety of experiments with the use of hydrogen peroxide, the process was carried out at 70 °C in the further tests.

Table 3. The influence of the amount of acetic acid and temperature on the course of the oxidation of TMP to TMBQ. Reaction conditions: TMP (5 mmol), 60% aq. H₂O₂ (20 mmol), [emim][OTf]-Al(OTf)₃, $\chi_{\text{Al(OTf)}_3} = 0.25$ (0.1 mol%), CH₃COOH.

Entry	CH ₃ COOH (cm ³)	Temperature (°C)	Time (h)	TMP ¹ Conversion (%)	TMBQ ¹ Selectivity (%)
1	1	70	2	77	78
2	1	70	4	99	84
3	3	70	2	79	79
4	3	70	4	91	81
5	1	100	2	99	86

¹ conversion and selectivity were measured using GC.

The concentration and the effect of the molar ratio of hydrogen peroxide to TMP were also studied (Table 4). The lower concentration of hydrogen peroxide (35% aq) reduced the catalytic efficiency due to the high water content and dilution of the reaction system. In turn, an increase in the molar ratio of H₂O₂ to TMP—with the optimal value 1:4—resulted in the increase in catalytic activity allowing 99% TMP conversion and 84% selectivity toward TMBQ.

Table 4. The influence of the concentration and amount of aqueous solution of H₂O₂ on the course of the oxidation of TMP to TMBQ. Reaction conditions: TMP (5 mmol), aq. H₂O₂, [emim][OTf]-Al(OTf)₃, $\chi_{\text{Al(OTf)}_3} = 0.25$ (0.1 mol%), CH₃COOH (1 cm³), 70 °C, 4 h.

Entry	Concentration of H ₂ O ₂ (%)	Molar Ratio of TMP:H ₂ O ₂	TMP ¹ Conversion (%)	TMBQ ¹ Selectivity (%)
1	35	1:3	87	77
2	60	1:3	95	81
3	60	1:2	77	82
4	60	1:4	99	84

¹ conversion and selectivity were measured using GC.

2.2. Heterogeneous System with Trifluoroaluminate Ionic Liquids

The heterogenisation of the catalyst is crucial for handling, separation, and recycling. From the other point of view, the process of anchoring ionic liquid onto the solid support (SILP, supported ionic liquid phase) can significantly reduce the required amount of ionic liquid as the catalyst. The most important advantages of SILPs at the molecular level are: the accessibility of acidic centres and the ability to tune the structure of the solid carrier with the emphasis on the high specific surface area and well defined pore size [23].

Taking advantage of the heterogeneous system in this work, ionic liquid [emim][OTf]-Al(OTf)₃, $\chi_{\text{Al(OTf)}_3} = 0.25$ was immobilised via the adsorption method on the surface of commercially available multiwalled carbon nanotubes (MWCNTs, CheapTubes). MWCNTs are very often used as versatile catalyst supports. Their properties, such as, e.g., large surface area, mechanical and thermal stability and small size, can significantly improve the activity and the selectivity of the catalysts supported on MWCNTs [24,25].

The catalyst was obtained by the simple mixing of the suspension of MWCNTs in *n*-hexane with [emim][OTf]-Al(OTf)₃ catalyst, $\chi_{\text{Al(OTf)}_3} = 0.25$ (mass ratio 2:1) in an ultrasonic bath for 2 h at room temperature. After the filtration and drying of the catalyst, the amount of the active phase supported on the surface of MWCNTs (9.1 wt.%) was determined using thermogravimetric analysis (TGA). The resulting MWCNT-[emim][OTf]-Al(OTf)₃ catalyst, $\chi_{\text{Al(OTf)}_3} = 0.25$, was used in the oxidation of TMP with 60% aq. H₂O₂ at 70 °C and compared to its soluble analogue using the same molar ratio of catalyst to TMP (0.1 mol% calculated per active phase) (Table 5).

Table 5. The influence of the type of catalyst based on trifluoroaluminate IL during the course of the oxidation of TMP to TMBQ. Reaction conditions: TMP (5 mmol), 60% aq. H₂O₂ (20 mmol), catalyst (0.1 mol%), CH₃COOH (1 cm³), 70 °C, 4 h.

Entry	Catalyst	TMP ¹ Conversion (%)	TMBQ ¹ Selectivity (%)	TON ² (10 ⁻³)	TOF ³ (min ⁻¹)
1	[emim][OTf]-Al(OTf) ₃ , χ _{Al(OTf)₃} = 0.25	99	84	83.2	347
2	MWCNT-[emim][OTf]-Al(OTf) ₃ , χ _{Al(OTf)₃} = 0.25	98	84	79.8	333

¹ conversion and selectivity were measured using GC; ² turnover number; ³ turnover frequency.

The obtained SILP catalyst exhibited high activity, similar to the catalytic activity of the homogenous ionic liquid. The turnover number (TON) and turnover frequency (TOF) values for MWCNT-[emim][OTf]-Al(OTf)₃, χ_{Al(OTf)₃} = 0.25 were comparable (TON 79,800 and TOF 333 min⁻¹) to those obtained for [emim][OTf]-Al(OTf)₃, χ_{Al(OTf)₃} = 0.25 (TON 83,200 and TOF 347 min⁻¹).

To investigate the possibility of recycling the SILP catalyst, the catalyst was filtered off after each reaction cycle, washed with *n*-hexane, and dried under vacuum (0.1 mbar) for 2 h. The recovery of the catalyst was very high and remained at the level of 95–99% in five reaction cycles.

Conversion and selectivity remained high in five cycles (Figure 4). A slight decrease in the activity was observed in the fourth reaction cycle, yielding 96% TMP conversion accompanied by 83% selectivity. The shape of the DTG (derivative thermogravimetry) curve after the fifth cycle in the range of 100–250 °C (Figure 5b) suggested the co-adsorption of other compounds of the reaction mixture on the surface of the MWCNTs, limiting the access to the active centres of the catalyst, mainly due to clogging the catalyst pores. Therefore, to calculate the amount of active phase after the fifth cycle, the range from 100 to 250 °C was not considered. The ionic liquid content decreased slightly after the fifth cycle to 8.7 wt.% compared to the fresh catalyst (9.1 wt.%).

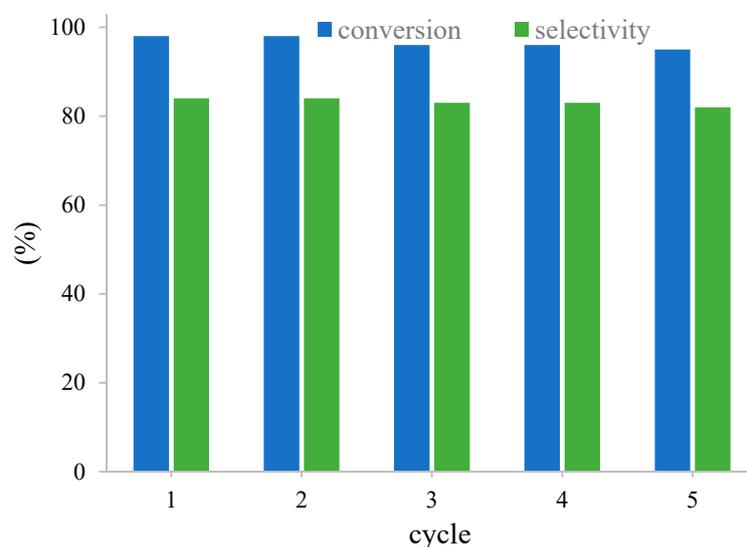


Figure 4. Recycling of multiwalled carbon nanotube (MWCNT)-[emim][OTf]-Al(OTf)₃, χ_{Al(OTf)₃} = 0.25. Reaction conditions: TMP (25 mmol), 60% aq. H₂O₂ (100 mmol), MWCNT-[emim][OTf]-Al(OTf)₃, χ_{Al(OTf)₃} = 0.25 (0.1 mol%), CH₃COOH (5 cm³), 70 °C, 4 h, conversion and selectivity were measured using GC.

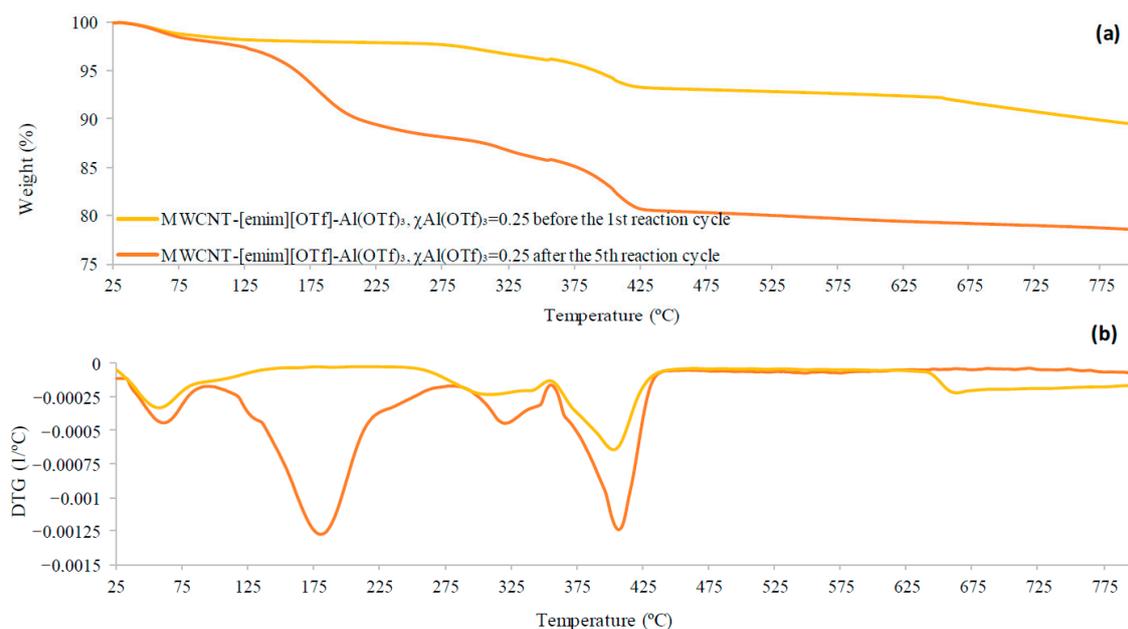


Figure 5. TGA and DTG curves, recorded in nitrogen (pyrolytic conditions), for the fresh catalyst MWCNT-[emim][OTf]-Al(OTf)₃, $\chi_{\text{Al(OTf)}_3} = 0.25$, and after the fifth cycle. (a) TGA curves; (b) DTG curves.

3. Materials and Methods

3.1. Materials

1-Ethyl-3-methylimidazolium triflate—[emim][OTf], Al(OTf)₃ (Sigma-Aldrich, St. Louis, MO, USA), 2,3,6-Trimethylphenol (98%) (Acros, Waltham, MA, USA) and MWCNTs (>95 wt.%, CheapTubes Inc., Grafton, VT, USA) were used.

3.2. Experimental Procedures

3.2.1. Homogenous Catalyst

Trifluoroaluminate ionic liquids were obtained according to the procedure described earlier [19]. Briefly, [emim][OTf] (2.60 g, 0.0100 mol) and Al(OTf)₃ in various molar ratios (0.84–1.58 g, 0.0018–0.0033 mol), were introduced into a 25 cm³ round-bottom flask sealed with a septum. The reactants were stirred (300 ppm) in the glove box at 85 °C for 2 h. The product was obtained in 99% yield as yellow liquid and was further used without purification.

3.2.2. Heterogeneous Catalyst

Ionic liquid [emim][OTf]-Al(OTf)₃, $\chi_{\text{Al(OTf)}_3} = 0.25$ (0.62 g, 0.02 mol), MWCNTs (1.24 g) and *n*-hexane (10 cm³) as a solvent were added to the round-bottom flask sealed with a septum, and stirred in an ultrasonic bath (25 °C, 2 h). Then, the heterogeneous catalyst was filtered through a Büchner funnel, washed with *n*-hexane (5 × 25 cm³). The catalyst was dried at 25 °C on a Schlenk line (0.1 mbar, 2 h).

3.2.3. Synthesis of 2,3,6-Trimethyl-1,4-Benzoquinone

General procedure: [emim][OTf]-Al(OTf)₃ or immobilised [emim][OTf]-Al(OTf)₃ (0.1–3.0 mol% in the respect to TMP), TMP (0.68 g, 5 mmol) and solvent (1–3 cm³) were added into a 25 cm³ two-neck round bottom flask equipped with a reflux condenser. Then, 35 or 60%_{aq} H₂O₂ (0.57–1.46 g, 10–20 mmol) was added. The reactants were stirred (1000 ppm) at 70–100 °C for 2–4 h under reflux. The reaction progress was monitored by GC.

Product isolation: [emim][OTf]-Al(OTf)₃, $\chi_{\text{Al(OTf)}_3} = 0.25$ used at 0.1 mol% per TMP, TMP (0.68 g, 5 mmol) and acetic acid as solvent (1 cm³) were added into a 25 cm³ two-neck round bottom flask equipped with a reflux condenser. Then, 60%_{aq} H₂O₂ (1.46 g, 20 mmol) was added. The reactants were stirred (1000 ppm) at 70 °C for 4 h under reflux. After the addition of *n*-hexane (10 cm³), [emim][OTf]-Al(OTf)₃ formed a second phase that was easy to separate. Then, the product was purified by column chromatography (silica; *n*-hexane:AcOEt 25:1, *v/v*). 2,3,6-trimethyl-1,4-benzoquinone was obtained as a yellow oil in 80% yield.

2,3,6-trimethyl-1,4-benzoquinone: ¹H NMR (400 MHz, CDCl₃) δ : 6.49 (q, *J* = 1,6 Hz, 1H), 1.97–1.96 (m, 3H), 1.96–1.95 (m, 3H), 1.95–1.93 (m, 3H). ¹³C NMR (150 MHz, CDCl₃) δ : 187.86, 187.47, 145.35, 140.91, 140.75, 133.09, 15.90, 12.38, 12.07. GC–MS: (EI) *m/z* (%) 150 (100, M⁺), 122 (30), 107 (42), 96 (18), 79 (29), 68 (31), 54 (17), 39 (27).

The heterogeneous catalyst MWCNT-[emim][OTf]-Al(OTf)₃ was recycled, $\chi_{\text{Al(OTf)}_3} = 0.25$. For the catalyst recycling tests, all reactants and reagents were used in 5-fold larger scale compared to screening tests. After the reaction, 15 cm³ of *n*-hexane was added to the reaction mixture. Then, the catalyst was filtered off and dried under vacuum on a Schlenk line (60 °C, 0.1 mbar, 2 h) and used in the next cycle of the reaction.

3.3. Analyses

TMBQ and ILs were analysed by NMR (¹H 400 MHz and ¹³C 150 MHz, tetramethylsilane was used as an internal standard. NMR spectra were recorded on Agilent 400-MR (Agilent Technologies, Santa Clara, CA, USA). ILs were analysed neat (capillaries with d₆-DMSO were used as an external lock).

Samples from the reaction mixtures were analysed on a gas chromatograph (SHIMADZU GC-2010 Plus, Shimadzu Corp., Kyoto, Japan) equipped with a Zebron GC column (ZB-5MSi, dimensions: 30 m × 0.32 mm, a film thickness: 0.25 μm film, Phenomenex, Torrance, CA, USA) and on a gas chromatograph coupled with a mass spectrometer (Agilent 7890C GC with a Agilent 5975C MS, Agilent Technologies, Santa Clara, CA, USA). A capillary column HP-5 MS (dimensions: 30 m × 0.25 mm, a film thickness: 0.25 μm film, Agilent Technologies, Santa Clara, CA, USA) was used as a GC column and an EI (70 eV) was used as an ionisation method.

Thermogravimetric curves of the heterogeneous catalysts were recorded on a Mettler-Toledo thermobalance STAR851 (Mettler-Toledo, GmbH., Greifensee, Switzerland). The analyses were performed in nitrogen (flow: 100 mL min⁻¹), at temperatures ranging from 25 to 800 °C, at the heating rate 20 °C min⁻¹. Al₂O₃ crucibles (70 μL) were used for samples (5–10 mg).

Turnover number (TON) and turnover frequency (TOF) were calculated according to formulae 1 and 2:

$$\text{TON} = \text{yield of TMBQ (\%)} \times \text{moles of TMP (mol)} \times \text{moles of the catalyst (mol)} \quad (1)$$

$$\text{TOF} = \text{TON/reaction time (min)} \quad (2)$$

4. Conclusions

In conclusion, highly active catalytic systems based on trifluoroaluminate ionic liquid were developed for the oxidation of TMP to TMBQ using hydrogen peroxide as the green oxidant. Due to the formation of a separate IL-phase in the reaction system and the free radical mechanism of the oxidation process, the use of acetic acid as a solvent was necessary—it caused the homogenisation of the reaction mixture and increased the selectivity of the product. The immobilisation of the ionic liquid on MWCNTs allowed for the development of a highly effective catalyst that can be easily separated by filtration and used in five reaction cycles without a significant decrease in activity. The presented catalyst, both in the form of trifluoroaluminate IL and its heterogeneous counterpart, is characterised by the high activity in the oxidation reaction with hydrogen peroxide (99% conversion and 84% selectivity), with the ability to recycle the catalyst as the largest advantage for the heterogeneous system.

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Conflicts of Interest: The authors declare no conflict of interest.

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