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Efficient Oxidation of 2,3,6-Trimethyl Phenol using Non-Exchanged and H^+ Exchanged Manganese Oxide Octahedral Molecular Sieves (K-OMS-2 and H–K-OMS-2) as Catalysts

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Abstract A new and efficient oxidation process of 2,3,6-trimethyl phenol to 2,3,6-trimethyl benzoquinone (TMQ) is reported forthwith using non-exchanged and H^+-exchanged manganese oxide octahedral molecular sieves (K-OMS-2 and H–K-OMS-2) as benign catalysts. The oxidation reaction is efficiently carried out using TBHP as oxidant and with catalytic amounts of OMS-2 achieving $>95\%$ conversion with excellent selectivity ($\sim 99\%$) to TMQ in 30 min.

Keywords TMP oxidation · Heterogeneous catalysis · Efficient oxidation

1 Introduction

Vitamin E finds extensive use in food, medicine, and healthcare products. α-tocophenol is the form of vitamin E known to meet human needs [1] and plays a vital role in protecting human cells from the damaging effects of free radicals thus acting to prevent various diseases, for instance, cardiovascular diseases and cancer [2]. In addition to its antioxidant role, vitamin E also plays an important role in the regulation of gene expression, cell signaling, and other metabolic processes [1].

Current industrial production of vitamin E involves condensation of isophytol (IP) with 2,3,6-trimethyl-1,4-hydroquinone (TMHQ) [3] obtained by hydrogenating TMQ as shown schematically in Fig. 1. The industrial production is carried out via oxidation of TMP with molecular oxygen or air in the presence of copper halides as catalysts [4–6]. Generally, TMQ is obtained from oxidation of TMP [7, 8]. The order of reactions involves para-sulfonation of TMP followed by its oxidation using stoichiometric amounts of commercial manganese dioxide. Several researchers have studied the oxidation step of the reaction scheme with the aim of reducing the overall steps involved as well as moving toward processes that are more environmentally friendly. One-step reactions have been explored employing different oxidants (molecular oxygen (O_2), hydrogen peroxide (H_2O_2) or tertiary butyl hydroperoxides (TBHP) [9−13]. Sun et al. [9, 10] describe an approach utilizing copper (II) chloride ($CuCl_2$) as homogenous catalysts in ionic liquid medium of 1-butyl-3-methylimidazolium chloride (BMIM-Cl) with n-butanol as a co-solvent. In that study, the yield of TMQ reached 98% with use of higher amounts of $CuCl_2$ gradually decreasing with reduction in the catalyst amount. Although molecular oxygen was utilized, this method required closed vessel, pressurized conditions (up-to 10 bars) to achieve the reported results. Baiker and coworkers [11] utilized $CuCl_2$ in the presence of $NH_2OH{\cdot}HCl$ co-catalyst with TBHP as the oxidant in place of molecular oxygen. In this approach the amount of $CuCl_2$ could substantially be reduced without substantial reduction in product yield, however, catalyst recovery is still a challenge. Interestingly, the solubility of $CuCl_2$ in the $CuCl_2$ system is not mentioned. $CuCl_2$ is highly soluble in aqueous media and has been reported elsewhere to have a solubility of 164 mg/100 g solution in a system involving 1-butyl-3-methylimidazolium hexafluorophosphate—[BMIM] PF6

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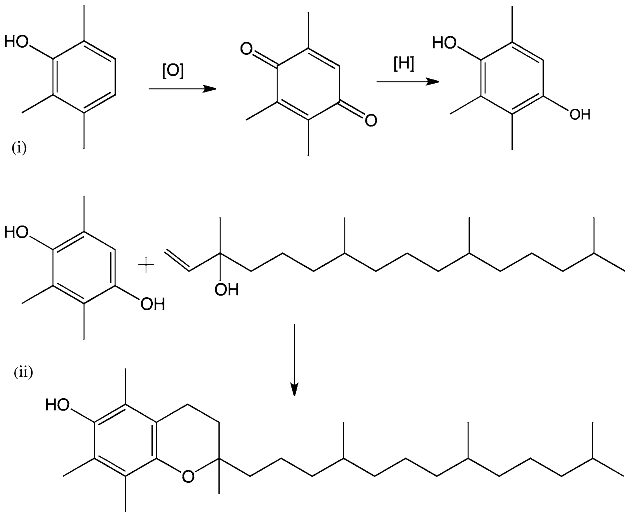

Fig. 1 Scheme showing steps involved in the current industrial production of vitamin E viz: (*i*) oxidation of TMP to TMQ and its subsequent reduction to TMHQ, and (*ii*) condensation of TMHQ with isophytol to form vitamin E

[12]. These solubility data imply that a similar trend is possible in the reported catalytic syntheses utilizing [BMIM]Cl, and thus homogeneous as opposed to heterogeneous species could be the active components of the afore-mentioned systems.

On the other hand, the use of molecular oxygen (under pressure) resulted in comparatively poor yields. Fenton's reagent [13] ($FeSO_4$/5% H_2O_2) system afforded 100% conversion with 99.9% selectivity to TMQ after a 3 h reaction period. Ti-based catalysts have also been studied for the synthesis of TMQ in a one-step reaction with high conversion and selectivities after a 30 min reaction period [14–19].

Herein, we report the benign oxidation of TMP to TMQ using K-OMS-2 and H–K-OMS-2 catalysts. These materials have previously been studied as selective catalysts for the oxidation of different organic compounds [20–25]. These materials showed excellent selectivity in the alcohol oxidation as well as in other catalytic systems.

2 Aim of Study

Given that K-OMS-2 materials have performed exemplarily in the oxidation of reported organic molecules, their performance in the oxidation of this important industrial chemical and the determination of the best reaction conditions are the driving forces of our current study. These aims are successfully realized, thus extending the applications of OMS-2 to include this important oxidation reaction.

3 Experimental

3.1 Reagents

Potassium permanganate ($KMnO_4$), manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$), 2,3,6-trimethyl phenol, acetonitrile (MeCN), and tert-butyl hydroperoxide (70% in water) were purchased from Sigma-Aldrich while concentrated nitric acid (HNO_3) was obtained from Alfa Aesar. All reagents were used without any further purification.

3.2 Catalyst Syntheses

Potassium containing OMS-2 (K-OMS-2) was synthesized using a variation of earlier reported procedures [26–28]. In a typical reaction, 42 mmol (6.65 g) $KMnO_4$ was added to 100 mL distilled-deionized water (DDW) to make mixture A. In another flask, 59 mmol (9.9 g) of $MnSO_4 \cdot H_2O$ was added to 33 mL DDW to make mixture B. Both A and B were stirred separately until complete dissolution of the reagents. To B, 3.4 mL of concentrated HNO_3 was added and further stirred. Solution A was transferred to a dropping funnel and drop-wise added to B under vigorous stirring. The resultant mixture was refluxed for 24 h in an oil bath maintained at 110 °C upon which the product was filtered, washed until neutral, dried in air at 120 °C for 12 h, and ground to fine powder. This powder (5 g) was ion-exchanged for H^+ by dispersing in 100 mL of 1 M HNO_3 and stirring at 70 °C for 6 h followed by a similar washing and drying procedure to form a strongly protonated H–K-OMS-2.

3.3 Catalytic Reactions

Catalytic oxidation reactions were performed by adding 1 mmol of TMP to 10 mL of acetonitrile that contained 50 mg catalyst and a given amount of TBHP as oxidant. Reactions were carried out at different temperatures for 30 min and samples withdrawn using a syringe fitted with an inline (0.45 μm) filter. The composition was analyzed and quantified using GC–MS based on their relative peak areas. Time and temperature studies were performed by withdrawing samples for analysis at different time intervals at given set temperatures.

3.4 Catalyst Leaching Test

To test whether the reaction was truly heterogeneous we performed the hot filtration test [29]. This test was performed at 65 °C with all the other reaction conditions similar to those of catalytic reactions tests as reported above. At exactly 5 min after start of reaction, all the liquid was drawn into a syringe and then released into a clean flask that had been maintained in a drying oven. An in-line filter was used to exclude solid materials and the hot filtrate reacted for a further 30 min at the same reaction conditions.

4 Characterization of the Catalysts

The catalysts were characterized using: X-ray diffraction (XRD), scanning electron microscope (FE-SEM), and Brunauer–Emmett–Teller (BET) surface area and pore size distribution measurements. Results of these characterizations were compared to those in literature reports.

4.1 X-Ray Diffraction

Powder XRD studies were performed using a Scintag XDS-2000 diffractometer having Cu Kα ($\lambda = 0.15406$ nm) radiation and operating at a beam voltage of 45 kV and a current of 40 mA. XRD data were collected continuously in the 2θ range of 5–75° at a scan rate of 1.0°/min and the crystalline phase identified using a JCPDS database card number 29-1020. XRD studies were performed on three catalyst materials: freshly synthesized K-OMS-2, H^+-exchanged H–K-OMS-2, and recycled K-OMS-2 that had previously been used in one reaction after a washing and drying procedure.

4.2 Scanning Electron Microscope

FE-SEM was performed on a Zeiss DSM 982 Gemini instrument with a Schottky emitter at an accelerating voltage of 2 kV and a beam current of 1 mA. The carbon tape mount method was used in sample mounting. Powder samples were finely ground and dispersed in absolute ethanol in a glass vial then ultra-sonicated prior to being dispersed on Au–Pd-coated silicon glass chips previously mounted onto aluminum stubs with a two-sided carbon tape and dried by vacuum desiccation prior to SEM studies.

4.3 BET Surface Area and Pore Size Distribution

These were performed using nitrogen sorption on a Micrometrics ASAP 2010 accelerated surface area system. Samples were degassed at 200 °C for 12 h prior to pore size distribution experiments which were carried out at 77 K. The specific surface area of the material was determined by the BET method.

5 Results

5.1 Catalyst Characterization

K-OMS-2, H–K-OMS-2, and regenerated K-OMS-2 were subjected to XRD studies to identify their crystal structure and crystallinity. Figure 2 shows the results from these diffraction studies. The XRD peaks could be indexed to the Q-phase of Cryptomelane-type manganese oxide (JCPDS card no. 29-1020) for all of the three samples. Electron microscopy experiments were performed on K-OMS-2 and are shown in Fig. 3 while nitrogen sorption isotherms and BET surface areas of K-OMS-2 are shown in Fig. 4. FE-SEM micrographs revealed a fibrous morphology while the BET surface area was 98 m^2/g well in line with previously reported results.

5.2 Catalytic Results

5.2.1 Effects of the Type of Catalyst and Oxidant on Oxidation of TMP

The effect of the type of catalyst was studied by comparing a similar amount of H–K-OMS-2 to K-OMS-2 in the

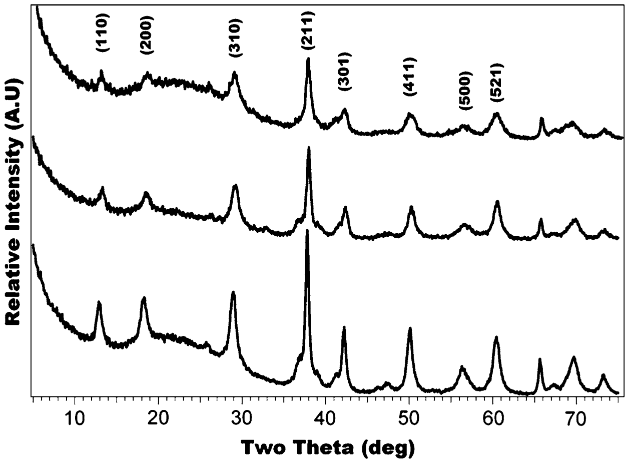

Fig. 2 X-ray diffraction patterns of as synthesized K-OMS-2 (*bottom*), H–K-OMS-2 (*middle*), and regenerated K-OMS-2 (*top*). All materials were indexed to the Q-phase of Cryptomelane (JCPDS card no. 29-1020)

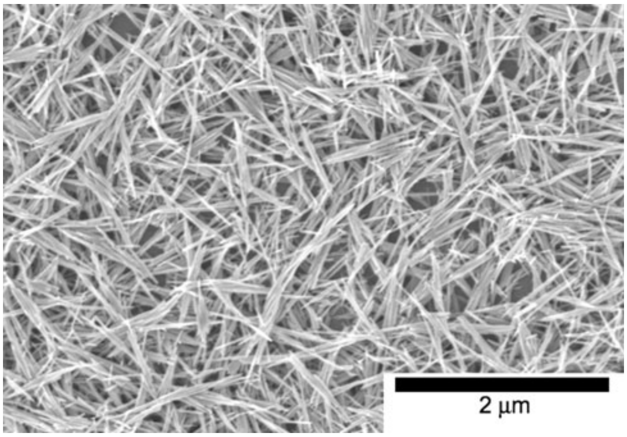

Fig. 3 FE-SEM micrograph images of the as-synthesized K-OMS-2 catalyst

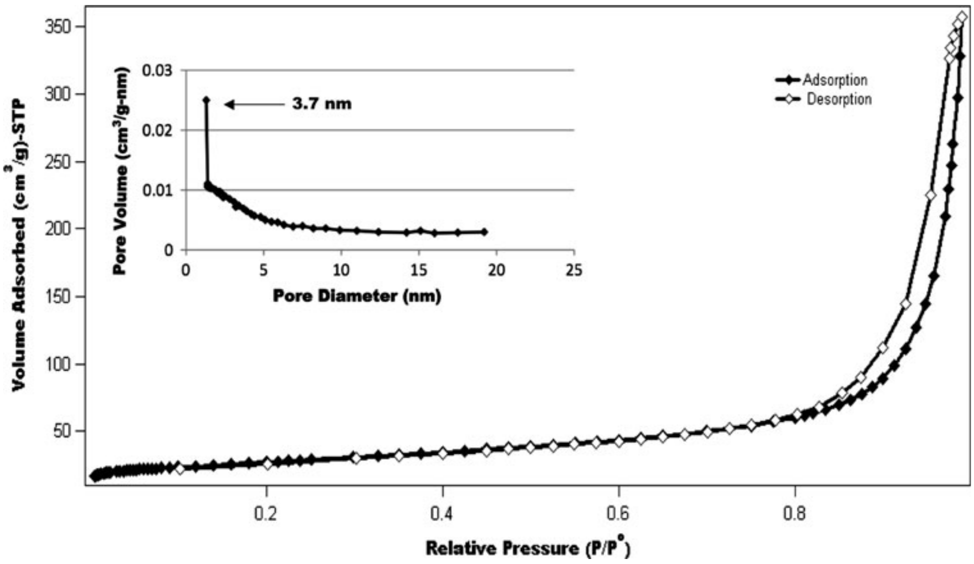

Fig. 4 Nitrogen sorption isotherms of the as-synthesized K-OMS-2 materials. Horvath–Kawazoe pore size distribution curve (*inset*). Corresponding BET surface area was 98 m^2/g

oxidation reaction. The effect of oxidant type was studied by comparing the results obtained by using molecular oxygen (present in air) or TBHP as oxidants. Also studied were: the effect of performing the catalytic tests under nitrogen atmosphere. The effect of the amount of TBHP was also studied. The results of these studies are summarized in Table 1.

5.2.2 Temperature and Reaction Time Effect

Temperature effect on the oxidation of TMP to TMQ was studied by performing the reactions at the best conditions experimentally determined of: 1 mmol substrate, 2 mmol TBHP in 10 mL of acetonitrile and 50 mg K-OMS-2 for 30 min. Different temperatures (room temperature, 40, 65, and 82 °C) were picked and the reactions monitored by analyzing the composition of samples withdrawn at short intervals over a 30 min duration using a syringe with an inline filter. The results of these studies are shown graphically in Figs. 5, 6, 7, 8.

5.2.3 Leaching Test Results

The results from the leaching test are shown in Table 1, entry 11. GC results of first filtrate had a conversion of 57% and after a 30 min filtrate reactions, stayed at 59% which is close to the first results and so can be assumed to be a constant.

Table 1 Effects of selected parameters on the oxidation of TMP

Entry	Catalyst loading (mg)	Oxidant amount (mmol)	TMP amount (mmol)	Temp. (°C)	Conv. (%)	Sele. (%)	TON
1	None	None	1	65	0	0	0
2	None	2.00$^{(a)}$	1	65	Trace	–	–
3	50	Nitrogen	1	65	6	0	1
4	50	Air	1	65	15	0	2
5	50	0.25	1	65	46 (35)	42 (45)	7 (6)
6	50	0.50	1	65	53	48	9
7	50	1.00	1	65	70	56	11
8	50	2.00	1	65	99	99	16
9	50$^{(b)}$	2.00	1	65	98	99	16
10	40	2.00	1	65	70	99	11
11$^{(c)}$	50	2.00	1	65	57 (59)	85 (87)	9 (9)

Percentage quantification (conversion and selectivity) was based on relative GC–MS peak areas (averaged for three injections) and confirmed using toluene as an internal standard to around 3% difference. Entry 1 corresponds to "blank" i.e. performed in the absence of catalyst. (–) was not determined due to the product peak being below the quantification range. All reactions were performed for 30 min except (a) for 60 min and (c) initially for 5 min. Similarly, all reactions were performed in the presence K-OMS-2 except (b) which was performed in the presence of H–K-OMS-2. Entry 5 (0.25 equivalent TBHP), a reaction under nitrogen purge gave results shown in the parenthesis. Hot catalyst filtration test results are shown in entry 11 with the final reaction results in parenthesis. Turnover number (TON) is the ratio of moles of substrate converted to moles of catalyst used. Unless noted, the oxidant used was TBHP

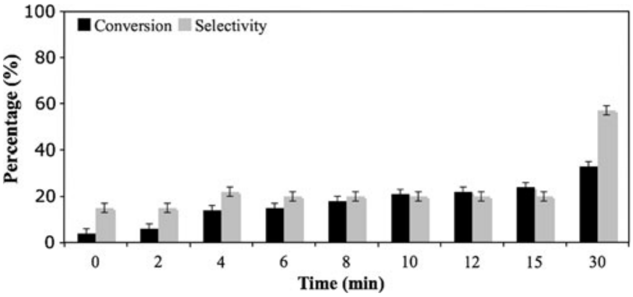

Fig. 5 Oxidation of TMP (1 mmol) at room temperature (25 °C) with 2 mmol TBHP in 10 mL acetonitrile and 50 mg of K-OMS-2

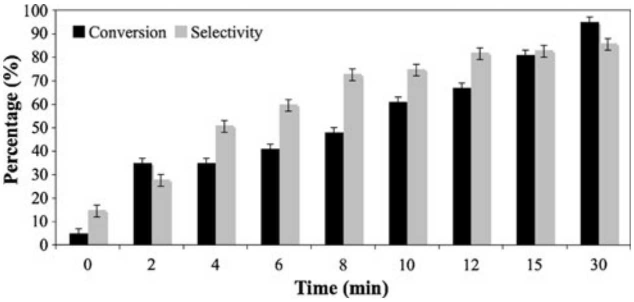

Fig. 6 Oxidation of TMP (1 mmol) at 40 °C with 2 mmol TBHP in 10 mL acetonitrile and 50 mg of K-OMS-2

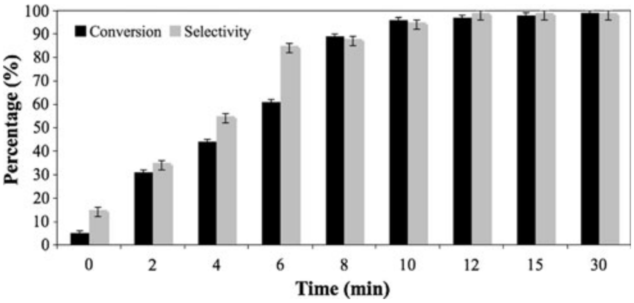

Fig. 7 Oxidation of TMP (1 mmol) at 65 °C with 2 mmol TBHP in 10 mL acetonitrile and 50 mg of K-OMS-2

6 Discussion

6.1 Catalyst Characterization

Pure, crystalline K-OMS-2 materials were successfully synthesized as evidenced by the XRD patterns that were indexed to the Q-phase of Cryptomelane (Fig. 2) and FE-SEM micrographs (Fig. 3). Ion-exchanging to prepare H–K-OMS-2 materials appears not to have a significant effect on the crystal structure (change in d-spacing or in the unit cell size) as identified from XRD patterns whose peak positions remain unchanged (not shifted) from those of K-OMS-2. This may indicate a lack of framework substitution and a possible exchange of the tunnel K^+ cations for H^+ ions. A regenerated K-OMS-2 retained the crystalline structure albeit with decreased peak intensities. Nitrogen sorption experiments reveal type-II isotherms due to an indefinite multilayer formation at higher relative pressure after complete formation of monolayer at lower relative pressure. Pore size distribution curves obtained using the Horvath–Kawazoe method indicate that the pore sizes are narrowly distributed at about 3.7 nm.

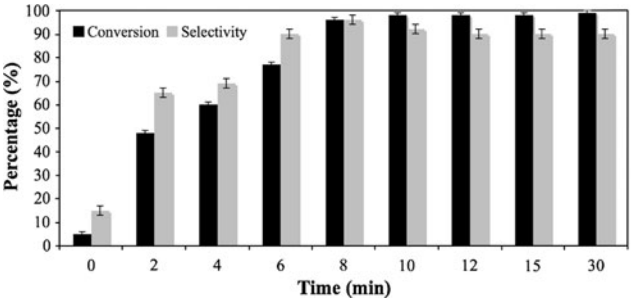

Fig. 8 Oxidation of TMP (1 mmol) at 82 °C with 2 mmol TBHP in 10 mL acetonitrile and 50 mg of K-OMS-2

6.2 Effect of Catalyst Nature on Oxidation of TMP

There is no significant difference between the performances of K-OMS-2 and protonated H–K-OMS-2 in the oxidation process, thus Brönsted acidity alone has no significant contribution to this oxidation reaction (Table 1, entries 8, 9) but rather, the active sites (manganese in different oxidation states) present on the catalyst and the oxidizing species (radical species from TBHP) present in solution play a more significant role. No oxidation occurred in the absence of the catalyst lending credence to the fact that this is indeed a reaction facilitated by the presence of K-OMS-2 (Table 1, entries 1 and 2). Furthermore, hot filtration of the catalyst and reacting the filtrate alone did not significantly change the conversion (Table 1, entry 11). Similar leaching studies using this catalyst for other oxidation studies have been reported [25]. The amount of K-OMS-2 used (50 mg, 0.0625 mmol) when compared to 1 mmol of substrate also suggests that this reaction is not stoichiometric either. Calculated turnover numbers (TON) are also above the threshold of 1 in stoichiometric reactions.

6.3 Role of Oxidant on Oxidation of TMP

The presence of oxidant plays a crucial role. In the absence of the oxidant, the reaction does not occur (Table 1, entry 1). Use of inert atmosphere (nitrogen) gave a conversion of 6% (Table 1, entry 3) while use of air gave a slightly higher conversion of 15% (entry 4). When TBHP was used, conversions of up-to 99% were obtained (Table 1, entries 5–9). At levels of 0.25–1 equivalent TBHP the conversion was low (46% no purge, 35% under nitrogen purge) and only reached the highest (99%) at two equivalent (Table 1, entries 5–8). This implies that dissolved oxygen also plays a role in the oxidation process. Conversion and selectivity obtained were highest when 50 mg of catalyst is used, two equivalent TBHP and the reaction carried out for 30 min. Thus the foregoing are the best-determined reaction conditions for this system. Recycled K-OMS-2 achieved a conversion of 70% when just 40 mg of the recycled catalyst is used in reaction (Table 1, entry 10). The reuse was achieved by scrapping the filtered catalyst off the filter paper, washing with ethanol and water then drying overnight at 120 °C.

6.4 Temperature and Reaction Time Effect on Oxidation of TMP

Conversion increased when temperature was increased from room temperature to 82 °C (Figs. 5, 6, 7, 8). As reaction time was increased at any given temperature, the conversion also increased. Time increase was limited to the first 30 min only. At room temperature, conversion increases from slightly below 5% at the start of the reaction to about 33% after 30 min (Fig. 5). At this temperature selectivity towards TMQ is poor. The other two products had a molecular mass of 270 but occurred at different retention times. 2,6-Dimethyl-4-[(2,4,6-trimethylphenoxy)methyl]phenol was a given possibility (from the database). At 40 °C, conversions steadily increase from 5 to 80% in the first 15 min reaching a high of 95% after 30 min (Fig. 6). At 65 °C, in as little as 10 min, the conversions reached over 95% and increased to 99% in 30 min (Fig. 7). At this temperature, selectivity rose to over 90% in the first 10 min. At 82 °C, the conversion was at 97% in 10 min and reached 99% after 30 min (Fig. 8). However, unlike at 65 °C where conversions were at 99%, at 82 °C the conversion or selectivity is constant at 90% by the end of the reaction.

7 Conclusion

From the foregoing, 65 °C is the optimum temperature for carrying out the oxidation of 2,3,6-trimethyl phenol using K-OMS-2 as benign catalysts. This temperature gave conversions of 99% and selectivity of 99% in 30 min of reaction time. Other optimum conditions are: 50 mg K-OMS-2, and 2 mmol TBHP for 1 mmol of TMP. These results are comparable to or better than reported [9–13, 30] results and are achieved using much milder and relatively inexpensive catalyst materials compared to literature reports. The heterogeneity of the catalyst towards this reaction was also confirmed to be truly heterogeneous.

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