

Review

tert-Butylation of hydroquinone with *tert*-butylphenols catalyzed by H-MCM-41

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Abstract

H-MCM-41 is an efficient and recyclable catalyst for the *trans tert*-butylation reaction between hydroquinone (HQ) and *tert*-butylphenols in a solvent free condition at 160 °C. *tert*-Butyl hydroquinone is the major product and 2,5-di-*tert*-butylhydroquinone (DTBHQ) is the minor product in this reaction. Among various *tert*-butylphenols tried, 2,6-di-*tert*-butyl-4-methylphenol is the best alkylating agent for hydroquinone.

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1. Introduction

tert-Butylhydroquinone (TBHQ) and 2,5-di-*tert*-butylhydroquinone (DTBHQ) are important phenolic anti-oxidants. TBHQ, in particular, has found widespread use as a food additive [1,2]. Both these additives are generally prepared by alkylation of hydroquinone (HQ) with *tert*-butanol or isobutylene [3] using mineral acids like phosphoric acid [4]. Methods are also reported for their preparation in a continuous mode [5]. *tert*-Butylation of aromatic ring can be effected using methyl *tert*-butyl ether as well [6]. Transalkylation of simple phenols is reported over heteropoly acids [7]. Our exploratory efforts for an eco-friendly route and other similar investigations led us to examine alkylation/transalkylation of HQ in presence of solid acid catalysts. During the course of our earlier work [8], we had observed de-*tert*-butylation and isomerisation in 2,6-di-*tert*-butylphenol (2,6DTBP) over solid acid catalysts. Interestingly, we observed that when HQ is added to the above system the mesoporous material H-MCM-41

catalyses the *trans tert*-butylation reaction of HQ with 2,6-di-*tert*-butylphenol prompting us, thereby, to investigate further.

2. Experimental

2.1. Materials

2,6-Di-*tert*-butylphenol, 2,4-di-*tert*-butylphenol (2,4DTBP (Fluka), *tert*-BuOH (Ranbaxy), HQ (Borregaard spa, Italy), 2,6-di-*tert*-butyl-4-methyl phenol (butylated hydroxytoluene, BHT), 2-*tert*-butyl-4-methylphenol (2TB4MP) (Quality Industries, Dhombivili, India) and di-*iso*-butylene (GPL, Baroda) were used as such having been checked for purity (GC) before use. Other chemicals were similarly checked for purity before use.

2.2. H-MCM-41

H-MCM-41 was synthesized as per earlier report [8]. Catalyst characterization was carried out as given in [8]. Partial dealumination of H-MCM-41 was carried out by steaming at 525 °C.

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2.3. SO_4^{2-}/ZrO_2

SO_4^{2-}/ZrO_2 was prepared by a method given in literature [9].

2.4. Acidity measurements

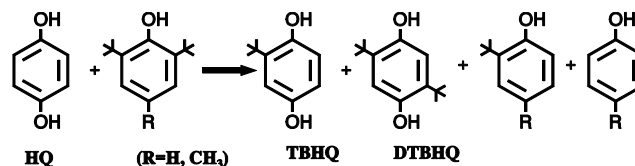
Acidity of H-MCM-41 samples was measured by NH_3 adsorption followed by temperature programmed desorption method [10].

2.5. Reaction procedure

The reaction was typically carried out in solvent free condition. In a 10 ml round bottomed flask was taken 2,6-DTBP (10 mmol), HQ (10 mmol) and H-MCM-41 (5 wt.%). The flask was fitted with a water condenser and closed with a N_2 balloon. The mixture was heated at $160^\circ C$ for 3 h with efficient stirring. After cooling, the reaction mixture was dissolved in petroleum ether ($60-80^\circ C$) and then in acetone. The catalyst was filtered, the filtrate concentrated and thereafter quantitatively analyzed by GC (Shimadzu 15A) using a 2 m long OV-17 column under temperature programmed heating. The products were identified by comparison with authentic samples. TBHQ was isolated by dissolving the reaction mixture in acetone, filtered to remove the catalyst, concentrated and then column chromatographed over silica gel (60–120 mesh) (Qualigens fine chemicals, Mumbai) using petroleum ether ($60-80^\circ C$) and dichloromethane as eluents in that order. TBHQ was eluted by dichloromethane fraction. The isolated products were characterized using elemental analysis, melting point and GC–MS (Finingan, UK).

3. Results and discussion

The role of phenolics as anti-oxidants in a variety of applications cannot be over estimated. The wide variety in structures [11] matches their differential activity as also in their synthetic methods. The alkylated phenols namely butylated hydroxytoluene and TBHQ remain the simpler yet effective



Scheme 1.

Table 2
Influence of reaction time on conversion and selectivity of products

No.	Time (h)	Conversion of 2,6-DTBP	Conversion of HQ	Selectivity	
				TBHQ	DTBHQ
9	1	21.9	14.8	95	5
9 ^a	1	20	16.9	100	–
10	2	80.6	67.5	84	16
11	3	76.3	–	79	21

2,6-DTBP: HQ = 1:1 (molar ratio); $160^\circ C$; H-MCM-41 ($SiO_2/Al_2O_3 = 15$) = 0.030 g.

^a Recycle run.

antioxidants. TBHQ, in particular, finds an important place among food-grade additives. Earlier, we had observed disproportionation, isomerisation and de-*tert*-butylation in the reaction of 2,6-DTBP over mesoporous H-MCM-41 material. This reaction pattern prompted us to examine the efficacy of 2,6-DTBP in the transalkylation of HQ to furnish TBHQ (Scheme 1).

As evidenced from Table 1, high HQ conversion (>90%) is observed at $160^\circ C$. Only in entry 5, low catalyst amount reduced both the 2,6-DTBP and HQ conversions. The catalyst acidity seems to have very little impact on the conversion as they all seem to be in the 91–99% range. TBHQ selectivity is maximum when the catalyst acidity is the highest (entry 7) and when reaction time is reduced by half (entry 6 versus entry 1). These differences appear significant and may be due to de-*tert*-butylation of DTBHQ formed under high acidic conditions or significant initial formation of TBHQ in short reaction time. Long reaction time (Tables 1 and 2) will only serve to increase the amount of DTBHQ. Percentage molar composition of products and reactants under different reaction times are given in Fig. 1. TBHQ

Table 1

Trans *tert*-butylation of hydroquinone with 2,6-DTBP catalyzed by H-MCM-41 of different acidity

No.	Catalyst (amount)	SiO_2/Al_2O_3	Acidity (mmol/g)	Conversion of 2,6-DTBP (%)	Conversion of HQ (%)	Products selectivity (%)	
						TBHQ	DTBHQ
1	H-MCM-41 (0.15 g)	30	0.811	–	92	78 (33.8)	22 (9.6)
2	H-MCM-41 (0.15 g)	60	0.77	93.2	86.9	83.6 (52.8)	16.4 (10.8)
3	–	–	NR	–	–	–	–
4	Steamed H-MCM-41 (0.15 g)	>60	0.688	98.9	95.2	79 (55)	21 (14.5)
5	H-MCM-41 (0.030 g)	30	0.811	86.0	85.3	83 (159)	17 (32.4)
6 ^a	H-MCM-41 (0.15 g)	30	0.811	98	91.3	95 (46)	5 (2.4)
7	H-MCM-41 (0.15 g)	15	0.891	97.5	91.3	94 (39)	6 (1.8)
8	SO_4^{2-}/ZrO_2 (0.15 g)	–	0.948	0	0	–	–

2,6-DTBP: HQ = 1:1 (molar ratio); $160^\circ C$; 3 h; values in the parentheses refer to turnover numbers (TON: mole of product formed/acidity of catalyst taken).

^a 1.5 h.

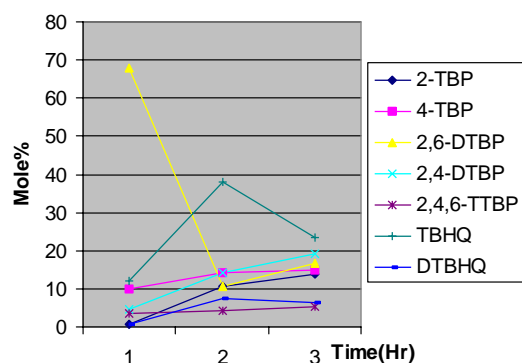


Fig. 1. Mol% composition of reaction mixture.

is the major component in the mixture. Yield of the product is high initially (2 h) and at higher reaction time (3 h) the concentration of this product is decreased. DTBHQ, 2-, and 4-TBP are all at equilibrium concentration (see Fig. 1). Yield of 2,4-DTBP is marginally increasing. The catalysts are consistently converting the alkylating agent 2,6-DTBP in high amounts. Other things being equal, low catalyst amount and short reaction time (entry 5 and 6) only seem to be increasing TBHQ selectivity (entry 1). Overall turnover number (TON) of the products depends on the acidity of the material. Increase in TON (entry 5) appears to correspond with decrease in catalyst amount taken. The catalyst is recyclable as evidenced by its activity after its filtration, washing, drying (100 °C for 0.5 h) and reuse (Table 2, entry 9^a).

The efficacy of other alkylated phenols as alkylating agents of HQ was studied. The results are given in Table 3 with alkylating agent and HQ ratio of 1:1 (entries 8, 9, 10 and 11). As can be seen, BHT provides highest HQ conversion with high TBHQ selectivity (entry 8). 2,4-DTBP and 2,6-DTBP behave similarly. 2-*tert*-Butyl-4-methylphenol (2TB4MP), with one *tert*-butyl group in comparison to other phenols gives about 46% HQ conversion—roughly half to that given in case of BHT, 2,4-DTBP and 2,6-DTBP. However, at 2TB4MP and HQ ratio of 2:1, the HQ conversion improves to match those in entries 10 and 11. This attests to the requirement of two *tert*-butyl groups in the alkyl phenol during trans-alkylation. Surprisingly the TBHQ selectivity reaches 100% under this condition.

Table 3
tert-Butylation of HQ with different *tert*-butylphenols

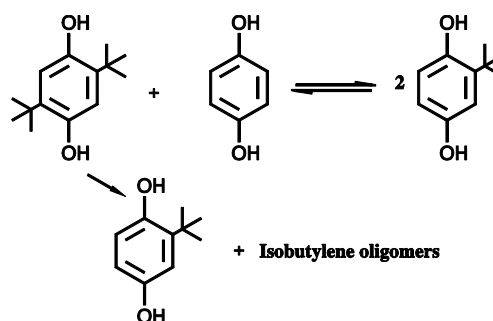
No.	Alkylating Agent	Alkylating agent/HQ	Conversion of HQ (%)	Product selectivity (%)	
				TBHQ	DTBHQ
8	BHT	1	99.8	92 (72.2)	8 (6.3)
9	2TB4MP	1	46.3	90 (46)	10 (5.2)
10	24DTBP	1	90	79 (61.6)	21 (15.8)
11	26DTBP	1	92	78 (33.8)	22 (9.6)
12	2TB4MP	2	89.3	100 (51.5)	–

160 °C; 3 h; H-MCM-41 (SiO₂/Al₂O₃ = 30) = 0.15 g.

Table 4
Effect of molar ratios of BHT and HQ on *tert*-butylation of HQ

No.	Ratio of BHT to HQ	Selectivity (%)		Conversion of HQ (%)
		TBHQ	DTBHQ	
13	1:1	92 (72.2)	8 (6.3)	99.8
14	1.5:1	65 (36.9)	35 (19.8)	94.2
15	1:1.5	81 (66.4)	19 (15.9)	87

Catalyst = H-MCM-41 (SiO₂/Al₂O₃ = 30) = 0.15 g; temperature = 160 °C; time = 3 h.



Scheme 2.

Despite this, entry 8 shows BHT as the best performing alkylating agent with high HQ conversion, 92% TBHQ selectivity and high turnover for the products. It was thus tempting to vary the reaction conditions using BHT to see if any further improvement takes place. Effect of BHT and HQ ratios was studied (Table 4). But, the other two ratios performed poorly in comparison with the 1:1 ratio of BHT and HQ.

4. Mechanism

In order to establish the mechanism of the reaction, few pilot experiments were carried out. When 2,6-DTBP was reacted with HQ in the absence of H-MCM-41 (Table 1, run 3) there was no reaction suggesting presence of catalyst is required. H-MCM-41 is a solid acid catalyst having different acidity values depending upon its SiO₂/Al₂O₃ ratio (Table 1). When steamed H-MCM-41 is used it shows higher conversion of HQ, selectivity and turn overs of

TBHQ and DTBHQ suggesting moderate acidity is required for the *tert*-butylation of HQ. When DTBHQ was reacted with HQ in 1:1 molar ratio with H-MCM-41 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 15$) at 160°C , 20% HQ is converted into TBHQ whereas 77% DTBHQ is converted into TBHQ. Both *trans tert*-butylation of HQ and *de-tert*-butylation of DTBHQ take place (Scheme 2) in presence of this strongly acidic catalyst. When strongly acidic $\text{SO}_4^{2-}/\text{ZrO}_2$ (acidity = 0.948 mmol/g [12]) is employed as the catalyst for the reaction between 2,6-DTBP and HQ at 160°C there was no trace of product. This clearly shows that the *trans tert*-butylation reaction takes place inside the channels of mesoporous material and the nature of acidic sites may be crucial in this reaction.

5. Conclusions

In conclusion, the study demonstrates that the mesoporous H-MCM-41 is an efficient catalyst in an eco-friendly route for *tert*-butylation of HQ leading to formation of TBHQ as the major product. Further, to our knowledge, this work shows for the first time that TBHQ can be synthesized by *trans tert*-butylation from *tert*-butylphenols and HQ in solvent free conditions.

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