

# Selective synthesis of 2-*t*-butylated hydroxyl anisole by *t*-butylation of 4-methoxyphenol with *t*-butyl alcohol over mesoporous solid acid catalysts

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## Abstract

*t*-Butylation of 4-methoxyphenol (4-MP) with *t*-butylalcohol (*t*-BuOH) as alkylating agent have been conducted under liquid phase reaction conditions over Zn–Al–MCM-41 catalysts with different  $n_{\text{Si}}/(n_{\text{Zn}} + n_{\text{Al}})$  ratios for selective synthesis of 2-*t*-butylated hydroxyl anisole (2-TBHA). The influences of various reaction parameters such as reaction temperature, time and *t*-BuOH to 4-MP ratios on the conversion of 4-MP and the selectivity of 2-TBHA have also been studied. With the decrease of the  $n_{\text{Si}}/(n_{\text{Zn}} + n_{\text{Al}})$  ratios of Zn–Al–MCM-41 catalysts from 380 to 75, the conversion of 4-MP as well as the yield and selectivity of 2-TBHA increase due to the increase of the number of Brønsted acid sites in Zn–Al–MCM-41 catalysts. The  $n_{\text{Si}}/(n_{\text{Zn}} + n_{\text{Al}})$  ratio of 75 is found to be the most suitable and reusable for the *t*-butylation of 4-MP with *t*-BuOH for selective synthesis of 2-TBHA.

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## 1. Introduction

The alkylation of phenol and its derivatives with different alcohols are industrially important as they are used for the production of a variety of organic products [1]. Among these, alkylation of 4-methoxyphenol with *tert*-butanol is used for the production of 2-TBHA, which is an important commercial antioxidant to stabilize food against auto-oxidation. Butylated hydroxy anisole (BHA), which is a commercial mixture of mono- and di-*tert*-butylated products of 4-MP, is an effective anti-oxidant in production industries such as foodstuffs [2], soaps [3], cosmetics [4], and pharmaceuticals [5,6]. BHA is also used to improve micro-suspension polymerisation process in producing homo- and co-polymers of vinyl chloride [7]. Moreover, BHA is proved to be a better anti-oxidant than butylated hydroxy toluene (BHT) and *n*-propyl gallate for food preservation [8].

BHA has been synthesized, by *t*-butylation of 4-MP using homogeneous Friedel–Crafts Lewis acid catalysts (such as

$\text{AlCl}_3$ ,  $\text{BF}_3$ ,  $\text{SbF}_5$ ,  $\text{ZnCl}_2$ ) and Brønsted acid catalysts (such as  $\text{H}_2\text{SO}_4$ , HF,  $\text{H}_3\text{PO}_4$ , HCl) [9], and by alkylation of 4-MP with *tert*-butanol [10,11] or *iso*-butylene [12,13] using orthophosphoric acid, and by alkylation of hydroquinone with *tert*-butanol using orthophosphoric acid as the catalyst followed by etherification with dimethyl sulphate in either methanolic sodium hydroxide [14,15] or aqueous sodium hydroxide solution [16] or aqueous sodium hydroxide solution with zinc dust [17,18]. However, the use of homogeneous catalysts gives rise to many problems concerning handling, safety, corrosion, and waste disposal. Waste generated in these industries ranges from 50 to 100 kg/kg of the desired product depending on the number of stages and type of functionality introduced in each stage. Since the presence of traces of impurities originating from the homogeneous catalysts cannot be tolerated in any chemical for food, pharmaceutical, fragrance and flavor applications, while, the cost of removal of these impurities becomes excessive. Furthermore, the prices of fine chemicals are so expensive and production volumes are so low that no serious attempts were made until recently to recover the catalyst or change the processes [20,21]. BHA has also been prepared by alkylating hydroquinone with *iso*-butylene over silica-alumina followed by etherification with dimethyl sulphate, which is again haz-

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ardous and polluting [19]. In order to avoid these problems, many efforts have been devoted to search of the solid acid catalysts that are more selective, safe, environmentally friendly, regenerable and reusable, and which do not have to be destroyed after reaction.

Therefore, considerable efforts have been made for the development of suitable heterogeneous catalysts for *t*-butylation of 4-MP. Many patents claim the synthesis of BHA from 4-MP using aluminium alkoxide of *m*-methoxyphenol [22], aluminium alkoxide of aliphatic alcohols [23],  $\gamma$ -alumina [24], silica–metal oxide–Lewis base [25–27] and lithium-doped silica–alumina [28,29]. Although zeolite has relatively large surface areas and different pore structure, however the performance of zeolite is limited by diffusional constraints associated with smaller pores. Hence, the need for present day heterogeneous catalysts in processing hydrocarbons with high molecular weights has led researchers to the search for better catalytic systems. These limitations were overcome after the discovery of mesoporous materials [30,31].

The discovery of the mesoporous material MCM-41 [30,31] has greatly enlarged the window of porous materials applicable as catalysts for organic reactions. Unfortunately, the acid strength of Al-MCM-41 resembles that of the amorphous silica aluminas rather than that of the more strongly acidic zeolites [32]. Although the material is valuable for many organic conversions [33,34], enhancement of its acidity is desirable to widen its application.

Several approaches have been aimed at increasing the acid strength of the mesoporous material. Kozhevnikov et al. have showed that heteropoly acids (HPA) supported on MCM-41 are good catalysts for several reactions [35–37]. However, the catalytic stability of this catalyst lack when it is used to produce polar products as well as concern about the dispersion of HPA on the support [38], while, the leaching of HPA from the support, prevents its use in industrial applications. Another approach is the use of sulphonic acid groups covalently attached to the MCM-41 pore wall via an organic spacer [39]. Selvaraj et al. [40–48] have recently reported the details of the synthesis and catalytic properties of some mesoporous solid acid catalysts for the synthesis of *p*-cymene, neroline, dypnone, DABCO, 4-*t*-butyltoluene, 2,6-bis(4-methylphenyl) pyridine, diphenylmethane and nopol. Alkylation of aromatics has also been investigated over mesoporous solid acid catalysts [41,49–51].

In the present study, Zn–Al-MCM-41 with  $n_{\text{Si}}/(n_{\text{Zn}} + n_{\text{Al}})$  ratios equal to 75, 151, 228, 304 and 380 have been synthesized using cetyltrimethylammonium bromide as the template under hydrothermal conditions and characterized according to the published method [45]. The catalysts have used for selective synthesis of 2-TBHA by the alkylation of 2-methoxyphenol using *t*-BuOH as the alkylating reagent. *t*-BuOH is chosen instead of isobutene owing to the low cost and extensive use of *t*-BuOH in industries. To the best of our knowledge, mesoporous Zn–Al-MCM-41 catalysts, for the first time, have been applied for selective synthesis of 2-TBHA. The effects of reaction temperature, time, *t*-BuOH to 4-methoxyphenol ratio and recyclability on the selectivity of 2-TBHA have been thoroughly investigated.

## 2. Experimental

### 2.1. Materials

The syntheses of Zn–Al-MCM-41 materials were carried out by hydrothermal method using sodium metasilicate ( $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ), cetyltrimethylammonium bromide ( $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+\text{Br}$ ), zinc chloride ( $\text{ZnCl}_2$ ), aluminum sulphate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) and sulphuric acid ( $\text{H}_2\text{SO}_4$ ). In order to study the formation of 2-TBHA by *t*-butylation of 4-methoxyphenol, the reagents *t*-BuOH ( $(\text{CH}_3)_3\text{C}-\text{OH}$ ) and 4-methoxyphenol ( $\text{C}_7\text{H}_8\text{O}_2$ ) were used. All chemicals (AR grade) were purchased from Aldrich & Co., USA.

### 2.2. Synthesis and characterization of Zn–Al-MCM-41

Zn–Al-MCM-41 with  $n_{\text{Si}}/(n_{\text{Zn}} + n_{\text{Al}})$  ratios equal to 75, 151, 228, 304 and 380 were synthesized and characterized; acidity measurements were done according to the published method [45].

### 2.3. *t*-Butylation of 4-methoxyphenol—experimental procedure for liquid phase catalytic reaction

0.2 g of freshly calcined Zn–Al-MCM-41 catalyst (calcined at 400 °C) was added into a mixture of *t*-BuOH and 4-methoxyphenol containing various mole ratios using 25 ml of 1,4-dioxane as the solvent. Each reaction was carried out in a stirred batch autoclave reactor (100 ml, Autoclave Engineers) with the speed of agitation kept at 800 rpm at reaction temperatures between 100 and 175 °C for different times (h). The reactor was flushed twice with nitrogen to replace air. The reactions were carried out at 150 psi autogeneous pressure. After reaction, the reactor was cooled down to 0 °C and the reaction products were recovered from the reactor.

The activity of Zn–Al-MCM-41 gradually decreased during reaction, and hence the catalyst needed to be regenerated. It was found that the catalyst could be reused simply by exhaustive washing with acetone at 40 °C followed by drying at 120 °C for overnight.

All samples of the reaction mixture were withdrawn periodically from the closed reactor and analyzed on a gas chromatograph (Perkin-Elmer Model 8500) equipped with a flame ionization detector and a 2 m × 0.003 m capillary column. The stationary phase used was 10% OV-17 supported on chromosorb WHP. The products of the reaction were identified by GC/MS (QP5000, Shimadzu) and by comparing with authentic samples. Conversion of 4-MP was defined as the percentage of 4-MP converted into products.

## 3. Results and discussion

### 3.1. Physicochemical characterization of Zn–Al-MCM-41

The synthesized Zn–Al-MCM-41 catalysts have been characterized using several techniques according to the published method [22]. The *d*-spacing value ( $d_{100}$ ) and unit cell parameter ( $a_0$ ) of Zn–Al-MCM-41 are observed to decrease with the

Table 1  
Physicochemical characterization of Zn–Al–MCM-41 materials

Catalysts	Zn content <sup>d</sup> (wt%)	Al content <sup>d</sup> (wt%)	<i>d</i> -spacing <sup>a</sup> (Å)	Unit cell parameter <sup>a</sup> , <i>a</i> <sub>0</sub> (Å)	Surface area <sup>b</sup> (m <sup>2</sup> /g)	Pore size <sup>b</sup> , <i>D</i> (Å)	Pore volume <sup>b</sup> (cm <sup>3</sup> /g)	Wall thickness <sup>c</sup> (Å)
Zn–Al–MCM-41(75)	0.123	0.220	37.91	43.77	820	22.8	0.852	20.97
Zn–Al–MCM-41(151)	0.060	0.123	38.41	44.35	867	25.6	0.893	18.75
Zn–Al–MCM-41(228)	0.040	0.079	38.91	44.92	912	27.0	0.944	17.90
Zn–Al–MCM-41(304)	0.031	0.060	39.98	46.15	970	29.3	0.963	16.85
Zn–Al–MCM-41(380)	0.020	0.049	41.09	47.44	1071	32.2	0.983	15.20

<sup>a</sup> Values obtained from XRD studies.

<sup>b</sup> Values obtained from N<sub>2</sub>-adsorption results.

<sup>c</sup> Wall thickness (*t*) = unit cell parameter (*a*<sub>0</sub>) – pore size (*D*).

<sup>d</sup> The results obtained from ICP-AES.

Table 2  
Brønsted acidity and Lewis acidity of Zn–Al–MCM-41 samples measured by FTIR spectroscopy combined with pyridine adsorption and desorption at different temperatures

Catalysts	Total acidity from TPD-pyridine studies (mmol pyridine g <sup>-1</sup> )	Brønsted acidity <sup>a</sup> (temperature (0 °C)) (μmol pyridine g <sup>-1</sup> )				Lewis acidity <sup>a</sup> (temperature (0 °C)) (μmol pyridine g <sup>-1</sup> )			
		27	100	200	300	27	100	200	300
Zn–Al–MCM-41(75)	0.103	27.5	20.3	18.2	13.5	40.3	35.6	30.5	25.3
Zn–Al–MCM-41(151)	0.095	23.4	19.2	16.3	12.4	38.3	30.3	27.3	23.5
Zn–Al–MCM-41(228)	0.076	19.5	17.3	14.2	10.3	25.4	24.5	24.3	20.2
Zn–Al–MCM-41(304)	0.055	17.4	15.4	12.4	6.7	20.6	20.4	20.3	18.3
Zn–Al–MCM-41(380)	0.035	14.3	13.2	9.5	5.3	17.7	15.3	14.5	15.6

Total acidity measured by TPD-pyridine.

<sup>a</sup> Values obtained from FTIR-pyridine studies.

increase of the metal-ions content (Table 1). FTIR studies show that zinc- and aluminum-ions can be incorporated into the hexagonal mesopores of Si-MCM-41 since the wavenumber of the antisymmetric Si–O–Si vibration bands (1096 cm<sup>-1</sup>) of Zn–Al–

MCM-41 are higher than those in Al-MCM-41 (1083 cm<sup>-1</sup>). This shift is attributed to the increase of the mean Si–O distance in the wall caused by the substitution of the small ionic radii of silicon by the larger ionic radii of zinc. The zinc- and

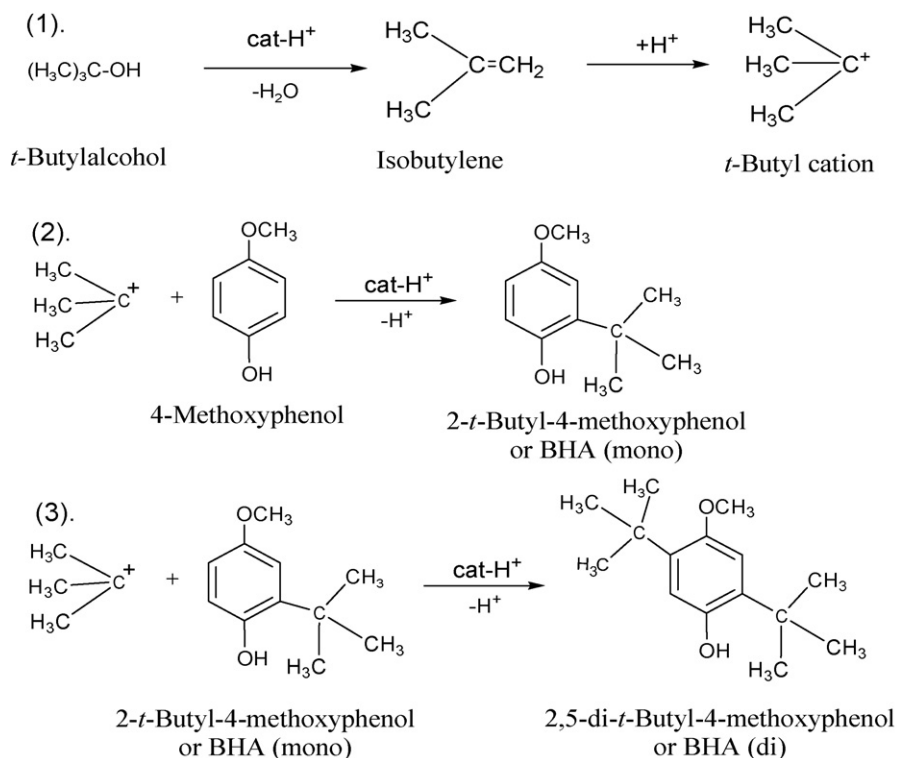


Fig. 1. Reaction scheme of *t*-butylation of 4-methoxyphenol.

Table 3  
Variation of reaction time with different  $n_{\text{Si}}/(n_{\text{Zn}} + n_{\text{Al}})$  ratios of Zn–Al-MCM-41 for *t*-butylation of 4-methoxyphenol

Catalysts	Time (h)	Conversion of 4-methoxyphenol (%)	Yield of products (%)		2-TBHA selectivity (%)
			2-TBHA	2,5-TBHA	
Zn–Al-MCM-41(75)	1	74.3	66.3	8	89.23
	2	92.2	91.9	0.3	99.67
	4	93.4	57.7	35.7	61.77
	8	96.2	53.4	42.8	55.50
Zn–Al-MCM-41(151)	1	96.2	60.8	8.4	87.86
	2	86.0	80.8	5.2	93.95
	4	88.7	52.2	36.5	58.85
	8	90.8	47.9	42.9	52.75
Zn–Al-MCM-41(228)	1	63.1	54.3	8.8	86.05
	2	79.8	72.8	7.0	91.22
	4	81.8	46.7	35.1	57.09
	8	84.4	42.4	42.0	50.23
Zn–Al-MCM-41(304)	1	56.0	45.8	10.2	81.78
	2	72.6	63.7	8.9	87.74
	4	74.5	41.2	33.3	55.30
	8	77.0	36.9	42.1	47.92
Zn–Al-MCM-41(380)	1	47.9	37.3	10.6	77.87
	2	64.7	52.6	12.1	81.29
	4	66.2	35.7	30.5	53.92
	8	68.6	31.4	37.2	45.77

Reaction conditions: 0.2 g of catalyst; reaction temperature ( $T$ ) = 150 °C; 2:1 mole ratio of *t*-BuOH to 4-methoxyphenol; speed, 800 rpm; solvent, 25 ml of 1, 4-dioxane; autogeneous pressure, 150 psi.

aluminum-ions content on the silica surface have been determined by ICP-AES (Table 1).  $^{27}\text{Al}$ -MAS-NMR studies show the incorporation of zinc- and aluminum-ions in tetrahedral and octahedral position on the silica surface, respectively, where the

$\text{Zn}^{2+}$ -ions are incorporated in the framework of Al-MCM-41, and the  $\text{Al}^{3+}$ -ions appear to be non-framework species on the silica surface when it is prepared under ion-exchange method [22]. SEM studies show that all calcined Zn–Al-MCM-41 catalysts

Table 4  
Variation of reaction temperature with different  $n_{\text{Si}}/(n_{\text{Zn}} + n_{\text{Al}})$  ratios of Zn–Al-MCM-41 for *t*-Butylation of 4-methoxyphenol

Catalysts	Temperature (°C)	Conversion 4-methoxyphenol (%)	Yield of products (%)		2-TBHA selectivity (%)
			2-TBHA	2,5-TBHA	
Zn–Al-MCM-41(75)	100	66.7	56.4	10.3	84.55
	125	75.3	66.3	9.0	88.04
	150	92.2	91.9	0.3	99.67
	175	93.6	59.4	30.9	63.46
Zn–Al-MCM-41(151)	100	61.4	50.7	10.7	82.57
	125	70.1	60.7	9.4	86.59
	150	86.0	80.8	5.2	93.95
	175	87.7	53.6	31.3	61.11
Zn–Al-MCM-41(228)	100	54.9	43.0	11.9	78.32
	125	63.8	53.1	10.7	83.22
	150	79.8	72.8	7.0	91.22
	175	80.8	45.8	32.5	56.68
Zn–Al-MCM-41(304)	100	47.5	33.3	14.2	70.10
	125	56.5	43.5	13.0	76.99
	150	72.6	63.7	8.9	87.74
	175	73.9	36.2	34.6	48.98
Zn–Al-MCM-41(380)	100	40.1	23.9	16.2	59.60
	125	49.2	33.9	15.3	68.90
	150	64.7	52.6	12.1	81.29
	175	65.0	26.5	36.5	40.76

Reaction conditions: 0.2 g of catalyst; reaction time ( $T$ ) = 2 h; 2:1 mole ratio of *t*-BuOH to 4-methoxyphenol; speed, 800 rpm; solvent, 25 ml of 1,4-dioxane; autogeneous pressure, 150 psi.

have either micellar rod-like shape hexagonal or spherical edge. Both pore channels and hexagonal symmetry can be clearly identified in the TEM image (not shown) for a large number of Zn–Al–MCM-41 samples, indicating that all these MCM-41 samples have only one uniform phase as inferred also from the XRD results. The surface area, pore diameter and pore volume of Zn–Al–MCM-41(75) are smaller than that of other Zn–Al–MCM-41 (Table 1) while the total Brønsted–Lewis acid sites in Zn–Al–MCM-41(75) are higher than that in other Zn–Al–MCM-41 (Table 2) due to a higher number of proton in Zn–Al–MCM-41(75) caused by the introduction of zinc ions into the framework of MCM-41 [22].

### 3.2. Mechanism of *t*-butylation of 4-MP

The *t*-butylation of 4-methoxyphenol with *t*-BuOH is an electrophilic substitution reaction on the aromatic ring. *t*-Butylation reactions catalyzed by acids or solid acid zeolites are commonly considered to proceed via carbenium ion mechanisms [26].

The reaction of 4-MP with *t*-BuOH is given in Fig. 1. *t*-BuOH reacts with solid acid catalyst to form isobutene, along with the removal of a water molecule (Eq. (1)). Isobutene is protonated by the solid acid catalyst to form *t*-butyl carbocation (Eq. (1)). The carbocation further reacts with 4-MP in the presence of the catalyst to form 2-TBHA (Eq. (2)), which then reacts with the similar type of carbocation over the catalyst to form 2,5-TBHA (2,5-*di-t*-butylated hydroxyl anisole) (Eq. (3)).

Based on this mechanism, two reaction products such as 2-TBHA and 2,5-TBHA are produced in the reaction. The mono-substituted product 2-TBHA is the main product because the second carbon-position is more favorable compared with the third and fifth carbon position due to the less steric hindrance of the methoxy group. The di-substituted product 2,5-TBHA is formed more than other di-substituted products because the second and fifth carbon positions are more favorable compared with the third and sixth carbon positions due to the less steric hindrance of the *t*-butylation. The effects of various reaction parameters on the *t*-butylation of 4-MP reaction have been investigated in this study.

### 3.3. Selectivity of 2-TBHA

The reaction of *t*-butylation of 4-MP was carried out in the presence of Zn–Al–MCM-41 catalysts having various  $n_{Si}/(n_{Zn} + n_{Al})$  ratios. Butylation of 4-MP is more activated on the *o*-position than the fifth position of carbon due to the presence of methoxy group in the *p*-position on the aromatic ring; however, the *t*-butyl cation is easily attacked on the *o*-carbon in aromatic ring using the catalytic removal of hydrogen. The maximum conversion of 4-MP (92.2%) and the maximum selectivity of 2-TBHA (99.67%) obtain when the reaction is carried out in the presence of Zn–Al–MCM-41(75). The conversion of 4-MP and selectivity of 2-TBHA in the presence of Zn–Al–MCM-41(75) are higher than those of other Zn–Al–MCM-41 due to the higher number of Brønsted acid sites which are generated from the creation of negative charges on the pore walls caused by the incorporation of

Zn-ions in place of tetrahedral Al-ions in the framework. The number of acid sites for different catalysts as obtained from TPD and FTIR-pyridine studies follow this order: Zn–Al–MCM-41(75) > Zn–Al–MCM-41(151) > Zn–Al–MCM-41(228) > Zn–Al–MCM-41(304) > Zn–Al–MCM-41(380). The results are shown in Table 2.

### 3.4. Variation of reaction time with different $n_{Si}/(n_{Zn} + n_{Al})$ ratios of Zn–Al–MCM-41

The liquid phase reaction of *t*-butylation of 4-MP under 2:1 mole ratio of *t*-BuOH to 4-MP and 25 ml of 1,4-dioxane as solvent was carried out at various reaction times at 150 °C in the presence of Zn–Al–MCM-41 catalysts with different  $n_{Si}/(n_{Zn} + n_{Al})$  ratio. The results are shown in Table 3. Based on the reaction results, lower reaction time (<1 h) does not favor the

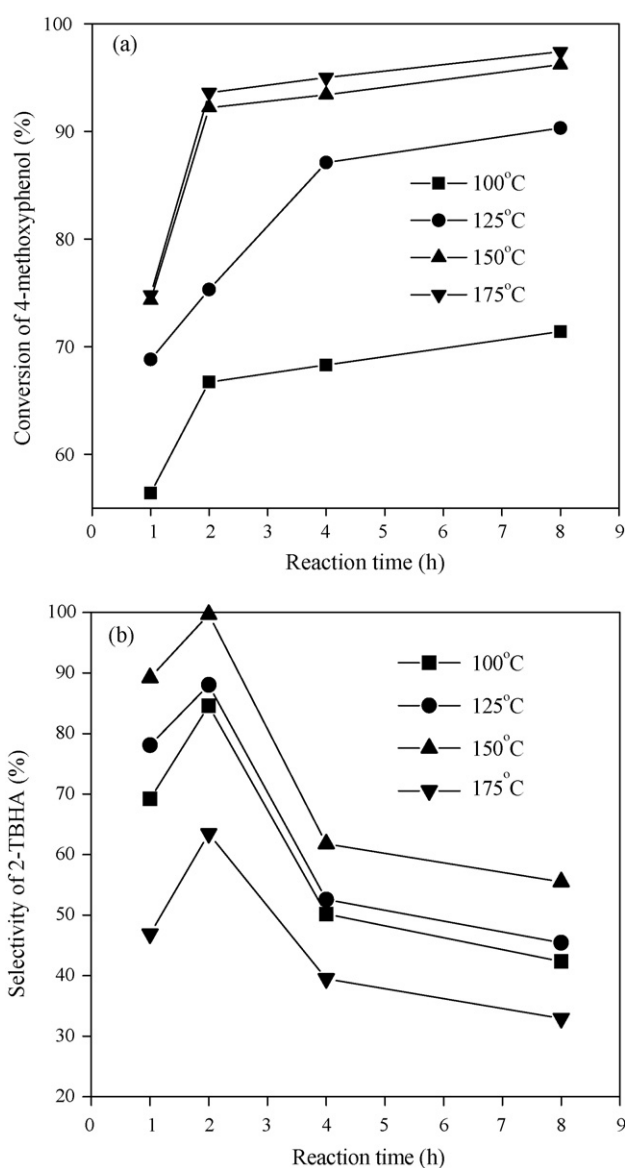


Fig. 2. Effect of reaction time on (a) the conversion of 4-methoxyphenol and (b) the selectivity of 2-TBHA over Zn–Al–MCM-41(75) at different reaction temperature.

formation of 2-TBHA because the reaction time is not enough for the reactants to react with the catalysts. An increase the conversion of 4-MP and a decrease the yield and selectivity of 2-TBHA is observed with the increase of reaction time up to 8 h (although the yield and selectivity increases from 1 to 2 h of reaction time). When the reaction time is increased >2 h, the conversion of 4-MP increases, but the yield and selectivity of 2-TBHA decreases, because 2-TBHA is gradually transformed to 2,5-TBHA by reacting with the excess of *t*-butyl carbocation. The optimum reaction time is thus found to be 2 h for the selective synthesis of 2-TBHA. Table 3 also shows that the conversion, yield and selectivity decreases with increasing  $n_{Si}/(n_{Zn} + n_{Al})$  ratios, possibly due to the fact that the number of acid sites on the catalyst surface decrease with the decrease of zinc and aluminum content. The conversion of 4-MP and selectivity of 2-TBHA are thus found to be higher in Zn–Al-MCM-41(75) than those in other Zn–Al-MCM-41 catalysts, possibly indicating that the greater chemisorption of reactants are on the catalyst surface pores by the higher number of zinc and aluminum content (Table 3).

### 3.5. Variation of reaction temperature with different $n_{Si}/(n_{Zn} + n_{Al})$ ratios of Zn–Al-MCM-41

The *t*-butylation of 4-MP was carried out for 2 h at various reaction temperatures using 2:1 mole ratio of *t*-BuOH to 4-MP and 25 ml of 1,4-dioxane as solvent in the presence of Zn–Al-MCM-41 catalysts with different  $n_{Si}/(n_{Zn} + n_{Al})$  ratio, and the results are shown in Table 4. An increase the conversion of 4-MP as well as the yield and selectivity of 2-TBHA is observed when the temperature is increased from 100 to 150 °C. From 150 to 175 °C, the conversion increases, but the yield and selectivity of 2-TBHA decreases due to the increase of the selectivity of 2,5-TBHA. The increase of the selectivity of 2,5-TBHA is attributed to the fact that 2-TBHA reacts with the excess carbocation with

the increase of reaction rate at higher reaction temperatures. Hence, the reaction results show that the optimum reaction temperature is found to be around 150 °C for the selective synthesis of 2-TBHA.

Fig. 2 shows the result of *t*-butylation of 4-MP over Zn–Al-MCM-41(75) under 2:1 mole ratio of *t*-BuOH to 4-MP and 25 ml of 1,4-dioxane at various reaction times and different reaction temperatures. When the reaction is performed for 2 h, an increase in the conversion of 4-MP as well as the yield and selectivity of 2-TBHA from 100 to 150 °C is observed. However, a slight increase in the conversion and a slight decrease in the selectivity for the same reaction temperature is observed with increasing reaction time (>2 h). Above 2 h, when the reaction time is further increased with increasing temperature (>150 °C), the conversion of 4-MP increases, but the selectivity of 2-TBHA decreases due to the increase of the selectivity of 2,5-TBHA.

### 3.6. Variation of *t*-BuOH to 4-MP ratios with different $n_{Si}/(n_{Zn} + n_{Al})$ ratios of Zn–Al-MCM-41

Table 5 shows the results of the *t*-butylation of 4-MP which was carried out at 150 °C for 2 h with various mole ratios of *t*-BuOH to 4-MP in the presence of Zn–Al-MCM-41 catalysts with different  $n_{Si}/(n_{Zn} + n_{Al})$  ratio. When the *t*-BuOH to 4-MP ratio is increased from 1:1 to 2:1, the conversion of 4-MP as well as the yield and selectivity of 2-TBHA increases. When the *t*-BuOH to 4-MP ratio is further increased from 2:1 to 6:1, the conversion of 4-MP as well as the yield and selectivity of 2-TBHA further decreases, possibly because the molar amount of 4-MP was not enough to react with the molar amount of *t*-BuOH. Generally, as the mole ratio of *t*-BuOH to 4-MP is increased, the conversion of 4-MP as well as the yield and selectivity of 2-TBHA decreases. In all cases, 2-TBHA is obtained as the major product along with a small amount of 2,5-TBHA as byproduct.

Table 5  
Variation of mole ratios (*t*-BuOH:4-methoxyphenol) with different  $n_{Si}/(n_{Zn} + n_{Al})$  ratios of Zn–Al-MCM-41 for *t*-Butylation of 4-methoxyphenol

Catalysts	<i>t</i> -BuOH/4-methoxyphenol mole ratio	Conversion 4-methoxyphenol (%)	Yield of products (%)		2-TBHA selectivity (%)
			2-TBHA	2,5-TBHA	
Zn–Al-MCM-41(75)	1:1	89.9	64.3	25.6	71.52
	2:1	92.2	91.9	0.3	99.67
	6:1	72.3	50.5	21.8	69.84
Zn–Al-MCM-41(151)	1:1	84.8	60.7	24.1	71.58
	2:1	86.0	80.8	5.2	93.95
	6:1	67.1	45.8	21.3	68.25
Zn–Al-MCM-41(228)	1:1	78.7	56.0	22.7	71.15
	2:1	79.8	72.8	7.0	91.22
	6:1	60.9	40.5	20.4	66.50
Zn–Al-MCM-41(304)	1:1	71.5	50.5	21.0	70.62
	2:1	72.6	63.7	8.9	87.74
	6:1	53.6	34.0	19.6	63.43
Zn–Al-MCM-41(380)	1:1	63.2	43.3	19.9	68.51
	2:1	64.7	52.6	12.1	81.29
	6:1	45.3	25.6	19.7	56.51

Reaction conditions: 0.2 g of catalyst; reaction temperature (*T*) = 150 °C; reaction time (*t*) = 2 h; Speed, 800 rpm; solvent, 25 ml of 1,4-dioxane; autogeneous pressure, 150 psi.

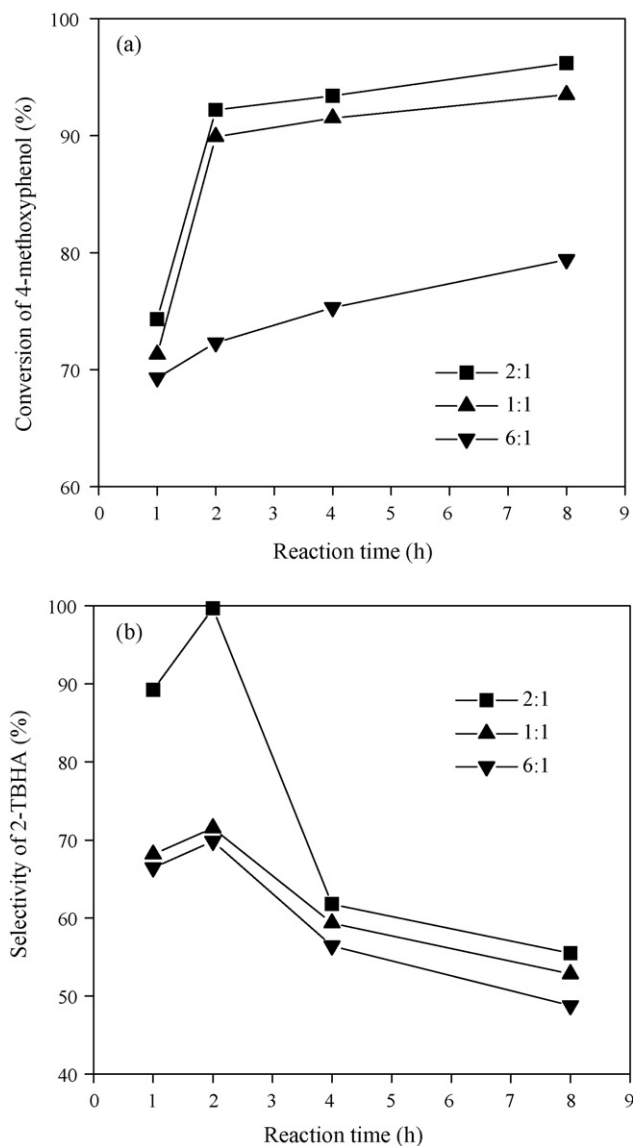


Fig. 3. Effect of reaction time on (a) the conversion of 4-methoxyphenol and (b) the selectivity of 2-TBHA over Zn-Al-MCM-41(75) at different mole ratios of *t*-BuOH to 4-methoxyphenol.

These results show that the highest conversion of 4-MP and the highest selectivity of 2-TBHA are obtained at *t*-BuOH to 4-MP ratio of 2:1 when the reaction is performed at 150 °C for 2 h over Zn-Al-MCM-41 catalysts with different  $n_{Si}/(n_{Zn} + n_{Al})$  ratios. Thus, the optimum reaction condition for obtaining the maximum conversion of 4-MP (92.2%) and the highest selectivity of 2-TBHA (99.67%) can be summarized as follows: the catalyst should be Zn-Al-MCM-41 with  $n_{Si}/(n_{Zn} + n_{Al}) = 75$ , the reaction should be performed at 150 °C for 2 h, and the *t*-BuOH to 4-MP ratio should be kept at 2:1.

Fig. 3 shows the result of *t*-butylation of 4-MP which was carried at 150 °C over Zn-Al-MCM-41(75) at various reaction times with different mole ratios of *t*-BuOH to 4-MP. Generally, the conversion of 4-MP increases when the reaction time is increased from 1 to 8 h. An increase in the selectivity of 2-TBHA is observed up to 2 h, but, the selectivity decreases at

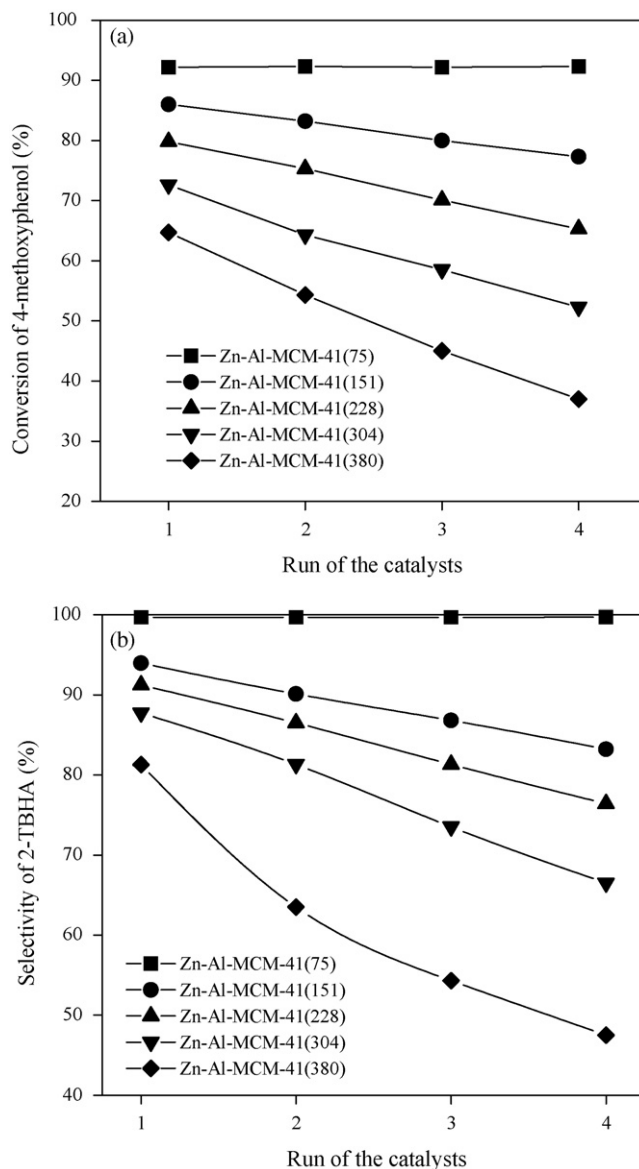


Fig. 4. Effect of the number of recycles of the used catalysts on (a) the conversion of 4-methoxyphenol and (b) the selectivity of 2-TBHA in the presence of different Zn-Al-MCM-41 catalysts.

higher reaction time (>2 h) in the following order of *t*-BuOH to 4-MP ratios: 6:1 < 1:1 < 2:1. The conversion and selectivity under this 2:1 mole ratio are the highest, possibly due to the presence of an equimolar of reactants on the Brønsted acid sites of catalyst surfaces.

### 3.7. Recyclability

All Zn-Al-MCM-41 catalysts were reused for the *t*-butylation of 4-MP which was performed at 150 °C for 2 h under 2:1 mole ratio of *t*-BuOH to 4-MP using 25 ml of 1,4-dioxane as the solvent. The results have been depicted in Fig. 4. No loss of the conversion of 4-MP and the selectivity of 2-TBHA can be observed after 4 recycles of Zn-Al-MCM-41(75). However, the conversion of 4-MP, as well as the yield and selectivity of 2-TBHA decreases continuously with the number of recycles for

other Zn–Al–MCM-41 catalysts under the same reaction conditions, probably due to the decrease of the catalytic activity resulting from the dehydration of Brønsted acid sites on the surface of these catalysts which have less zinc and aluminum content.

#### 4. Conclusions

Selective synthesis of 2-TBHA have been carried out over a series of Zn–Al–MCM-41 catalysts under different optimal reaction conditions. When the  $n_{Si}/(n_{Zn} + n_{Al})$ -molar ratios are increased, the conversion of 4-MP as well as the yield and selectivity of 2-TBHA decrease. A higher yield and selectivity of 2-TBHA and conversion of 4-MP using Zn–Al–MCM-41(75) depicts its superiority in performance as compared with other Zn–Al–MCM-41 catalysts. Furthermore, the Zn–Al–MCM-41(75) catalyst can be reused at least for four times for the *t*-butylation of 4-MP under 2:1 mole ratio of *t*-BuOH to 4-MP and 25 ml of 1,4-dioxane as solvent at 150 °C for 2 h without the lost of the conversion of 4-MP and the selectivity of 2-TBHA.

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