Highly selective synthesis of *t*-butyl-*p*-cresol (TBC) by *t*-butylation of *p*-cresol with *t*-butyl alcohol over microporous and mesoporous catalysts

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Abstract

A much green synthesis method is discovered for the synthesis of *t*-butyl-*p*-cresol (TBC), an important used as antioxidant in food industries and the basic raw material for the manufacture of oil-soluble phenol–formaldehyde resins. The TBC is synthesized with a conversion (93.2%) and selectivity (98.6%) through a heterogeneous *t*-butylation of *p*-cresol with *t*-butyl alcohol (*t*-BuOH) in the liquid phase over mild strong acid catalyst, Zn–Al-MCM-41(75). The catalytic results have also compared with those obtained using other Zn–Al-MCM-41, Al-MCM-41, HY, Hβ, H-mordenite and H-ZSM-5 zeolites. Based on the catalytic results, Zn–Al-MCM-41(75) is found to be a highly active and recyclable heterogeneous catalyst for selective synthesis of TBC.
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Keywords: Synthesis of solid acid catalysts; Catalytic activity; Acidity; Recyclability; Conversion of *p*-cresol; Selectivity of TBC

1. Introduction

Butylated hydroxytoluene (BHT) is a well known antioxidant, and it has been synthesized by *t*-butylation of *p*-cresol using *t*-butanol or isobutene as the alkylating agent over Friedel–Crafts catalysts such as AlCl$_3$, FeCl$_3$ and ZnCl$_2$ [1]. The use of homogeneous catalysts gives rise to many problems concerning a high corrosiveness, tedious work-up, requirement of stoichiometric quantities, the presence of several undesirable side products, and non-recycling of catalyst, and thus are highly non-ecofriendly. The major goals of 'green chemistry' are to increase process selectivity, maximize the use of starting materials, and to replace hazardous and stoichiometric reagents with eco-friendly catalysts in order to facilitate easy separation of the final reaction mixture, including recovery of the catalyst and also reusable. Therefore, some solid acid catalysts are used for *t*-butylation of *p*-cresol. Solid acid catalysts such as cation-exchange resins have been used as catalysts to this reaction [2,3]. Although, cation-exchange resin catalysts are environmental friendly, they have the disadvantages like low activity and less stability at

high temperatures [4]. Therefore, considerable efforts have been made for the development of suitable heterogeneous catalysts.

Butylation of *p*-cresol has been carried out with isobutylene as an alkylating agent using sulfated zirconia and zirconia-supported heteropoly acids [5,6]. Sulfated zirconia is then proved to be a highly active solid acid catalyst [7]. But, its poor stability and tendency to form volatile sulfur compounds during catalysis and regeneration limit its applicability [8]. Although, zirconia-supported heteropoly acid (HPA) is good catalysts for this reaction, it has a main drawback, that is why, it is easily leached from the support due to lack its stability, and prevents its use in industrial applications [9]. In this reaction the both C- and O-alkylated products have been formed. Based on the reaction results, it is observed that the C- and O-alkylated products are formed depending on reaction conditions (reaction temperature and type of the catalysts). Based on the literature results for this reaction, some catalysts with strong acidic sites or high reaction temperature lead to the formation of C-alkylated products, while, catalysts with weak acidic sites or low reaction temperature lead to the formation of O-alkylated products while some solid acid catalysts afford a less conversions and high selectivities [7]. Moreover, the need for the present day heterogeneous catalysts in processing hydrocarbons with high molecular weights has led researchers to better conversions and selectivities. These limita-

tions were overcome with the discovery of mesoporous materials [10] which have greatly enlarged mesopores suitable as catalysts for organic reactions involving bulky molecules. Unfortunately, the acid strength of MCM-41 resembles that of the amorphous silica aluminas rather than that of the more strongly acidic zeolites [11,12]. Although the mesoporous material is valuable for many organic conversions [13], enhancement of its acidity is desirable for extension of its applicability.

Several synthesis methods have been approached to increase the acid strength of the mesoporous materials. For example, MCM-41 materials have been synthesized using heteropoly acids (HPA) and sulfonic acid [14,15]. Selvaraj et al. have recently reported the details of the synthesis and characterization of several mesoporous catalysts with increasing acid strength, and used for the synthesis of fine chemicals along with 'a goal of green chemistry' [16–26]. The synthesis of mesoporous UDCaT catalyst (combination of hexagonal mesoporous silica (HMS) and sulphate modified zirconia material) have also been reported and used for the synthesis of TBC using methyl *tert*-butyl ether as the alkylating agent [27].

Recently, there has been an increasing interest in developing catalytic reaction processes with minimal environmental threats and maximal economical benefits. Hence, there has been a great demand to develop highly selective heterogeneous catalyst with a large number of Bronsted acid sites suitable for mild reaction conditions without employing toxic materials. To the best of our knowledge, there are currently no reports on the heterogeneous catalytic reaction for the *t*-butylation of *p*-cresol over Zn–Al-MCM-41. Herein we disclose the report of selective synthesis of TBC using Zn–Al-MCM-41 catalyst under mild reaction conditions. The catalytic results of Zn–Al-MCM-41 for selective synthesis of TBC are also correlated and compared with other solid catalysts, such as Al-MCM-41, USY, Hβ, H-ZSM-5 and H-mordenite.

2. Experimental

Zn–Al–MCM-41 with different $n_{Si}/(n_{Zn} + n_{Al})$ ratios and Al-MCM-41(21) were synthesized and characterized according to the published method [21]. Hβ ($n_{Si}/n_{Al} = 20$, Strem); HY ($n_{Si}/n_{Al} = 2.9$, PQ); H-mordenite ($n_{Si}/n_{Al} = 20$, PQ) and H-ZSM-5 ($n_{Si}/n_{Al} = 30$, PQ) were obtained from commercial sources. These catalysts were then calcined at 500 °C in air for 6 h before catalytic reaction.

A 0.2 g of catalyst was added into a mixture of *t*-BuOH/*p*-cresol in various mole ratios. Each reaction was carried out in

a stirred batch autoclave reactor (100 ml, autoclave engineers) at reaction temperatures between 30 and 120 °C for different times (h) while the speed agitation for this reaction was kept at 650 rpm. The reactor was flushed twice with nitrogen to replace air. Alkylation reactions were carried out at the autogeneous pressure. The reactor was cooled down to 0 °C and the reaction products were recovered from the reactor.

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. A 2 m × 0.003 m column was used. The stationary phase 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 was defined as the percentage of *p*-cresol converted into products.

Initially, all catalysts usually suffer from the catalytic activity and hence the catalyst needs to be regenerated by calcination. It can be recycled after exhaustive washing with acetone at 40 °C to remove the organics and unreacted reactants. Further the catalyst was washed at five times in a similar procedure. It was then dried at 200 °C overnight in air. The recycled catalyst was again prepared with a similar manner.

3. Results and discussion

3.1. Physico-chemical characterization of Zn–Al-MCM-41

The mesoporous Zn–Al-MCM-41 and Al-MCM-41(21) catalysts have been characterized using several sophisticated instrumental techniques according to the published method [21]. Based on the physico-chemical characterization results, the *d*-spacing value (d_{100}) and unitcell parameter (a_0) of Zn–Al-MCM-41 are observed to decrease with the increase of the metal-ions content (Table 1). FT-IR studies show that zinc- and aluminium-ions are incorporated into the hexagonal mesoporous Si-MCM-41 materials, however, the wavenumber of the antisymmetric Si-O-Si vibration bands (1096 cm^{-1}) in Zn–Al-MCM 41 are higher than those in Al-MCM-41 (1083 cm^{-1}). The 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 aluminum-ions content on the silica surface have been determined by ICP-AES (Tables 1 and 3). ^{27}Al–MAS-NMR studies show that the incorporation of zinc- and aluminum-ions are in tetrahedral and octahedral position on the silica surface, respectively,

Table 1
Physico-chemical characterization of Zn–Al-MCM-41

Catalysts	Zn content (wt%)[a]	Al content (wt%)[a]	d_{100} (Å)	a_0 (Å)	SA$_{BET}$ (m^2/g)	D_p (Å)	V_p (cm^3/g)	t_w (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
Al-MCM-41(21)	–	0.499	38.41	44.35	830	27.5	0.866	16.85

[a] Results obtained from ICP-AES.

Table 2
Bronsted acidity and Lewis acidity of the Zn–Al-MCM-41 as characterized by FT-IR pyridine adsorption and desorption measurements at different temperatures as well as total acidity measured by TPD-pyridine

Catalysts	Total acidity (μmol pyridine g^{-1})[a]	Bronsted acidity (μmol pyridine g^{-1})[b]				Lewis acidity (μmol pyridine g^{-1})[b]			
		25 °C	100 °C	200 °C	300 °C	25 °C	100 °C	200 °C	300 °C
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
Al-MCM-41	0.099	23.8	18.3	12.3	11.3	11.9	10.3	8.3	6.3

[a] Results obtained from TPD-pyridine.
[b] Results obtained from FT-IR pyridine.

where the Zn^{2+}-ions could be incorporated in the framework of Al-MCM-41 by non-framework octahedral Al^{3+}-ions species on the silica surface when it is prepared under ion-exchange method [21]. SEM studies show that all calcined Zn–Al-MCM-41 and Al-MCM-41(21) catalysts have either micellar rod-like shape hexagonal or spherical edge. Both pore channels and hexagonal symmetry can be clearly identified in the TEM image for a large number of Zn–Al-MCM-41 and Al-MCM-41(21), indicating that all these MCM-41 samples have only one uniform phase as inferred also from the XRD results. The surface area (SA$_{BET}$), pore diameter (D_p) and pore volume (V_p) of Zn–Al-MCM-41(75) are smaller than that of other Zn–Al-MCM-41 and Al-MCM-41(21) (Table 1) while the total and Bronsted–Lewis acid sites in Zn–Al-MCM-41(75) are higher than that in other Zn–Al-MCM-41 and Al-MCM-41(21) due to increasing protons with the aluminium ions non-framework by the introduction of zinc ions [21], and the values are shown in Table 2.

The synthesized Zn–Al-MCM-41, Al-MCM-41 and some commercial catalysts (HY, Hβ, H-mordenite and H-ZSM-5) have been used for *t*-butylation of *p*-cresol with *t*-BuOH for selective synthesis of TBC. The reaction mechanism is described in the next section.

Scheme 1. *t*-Butylation of *p*-cresol reaction over solid acid catalysts.

3.2. Mechanism of t-butylation of p-cresol

The *t*-butylation of *p*-cresol 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 [23].

t-BuOH reacts with solid acid catalyst to form isobutene, along with removal of water (Eq. (1)). Isobutene is protonated by the catalyst to form *t*-butyl carbocation (Eq. (1)). The carbocation further reacts with *p*-cresol in the presence of the catalyst to form TBC (Eq. (2)). TBC reacts with the similar type of carobocation over the catalyst to form DTBC (Eq. (3)). Excess isobutylene further reacts with each molecule over the catalyst to form diisobutylene (Eq. (4)) while the diisobutylene react with excess isobutylene in the presence of the catalyst to form tri-isobutylene (Eq. (5)). All the above products (all equations) are obtained with respect to the catalytic properties along with optimal reaction conditions. The reaction of *p*-cresol with *t*-BuOH is given in Scheme 1.

In all cases, the main reaction product TBC has been identified. Only the trance amount byproducts like DTBC, diisobutylene and triisobutylene is also present in the reaction. The main product is logically TBC because second and sixth carbon-position are more favourable compared with the other carbon positions due to the less steric hindrance of the hydroxyl group while some byproducts such as DTBC, diisobutylene and tri-isobutylene are formed with respect to optimal conditions and acid strength of the catalysts. The effects of various parameters on the *t*-butylation of *p*-cresol reaction are thoroughly studied.

3.3. Selectivity of TBC

The *t*-butylation of *p*-cresol for the synthesis of TBC (Fig. 1) was carried out with 2:1 mole ratio of *t*-BuOH to *p*-cresol at 90 °C for 2 h over H-ZSM-5(15), H-mordenite(20), Hβ(20), HY(2.6), Al-MCM-41(21), Zn–Al-MCM-41(75), Zn–Al-MCM-41(151), Zn–Al-MCM-41(228), Zn–Al-MCM-41(308) and Zn–Al-MCM-41(380) catalysts and their results are shown in Table 3. The order of catalytic activity for selectivity of TBC are found to be as follows: Zn–Al-MCM-41(75) > Zn–Al-MCM-41(151) > Zn–Al-MCM-41(228) > Al-MCM-41 (21) > Zn–Al-MCM-41(308) > Zn–Al-MCM-41(380) > HY (2.6) > Hβ(20) > H-mordenite(20) ≥ H-ZSM-5(15). Based on the literature results reporting the FT-IR analysis of the adsorbed pyridine and ammonia–TPD [28], the acid strength of the catalysts also follow a similar trend except for H-ZSM-5 zeolite. Zeolite Hβ, which has a 30.4% *p*-cresol conversion, is found to be more active than HY, which has a 25.3% *p*-cresol conversion. However, in terms of selectivity, Hβ is found to be less selective (74.50%) than HY (80.40%). The higher selectivity of HY might be attributed to its strong acidity and slightly larger pore opening size (7.4 Å) than Hβ (7.6 and 5.4 Å) as geometrical constraints by Hβ, did not allow the formation of bulkier products in the small channels, and hence a higher selectivity of TBC is achieved over HY rather than Hβ zeolite. In contrast, H-mordenite and H-ZSM-5, in spite of its
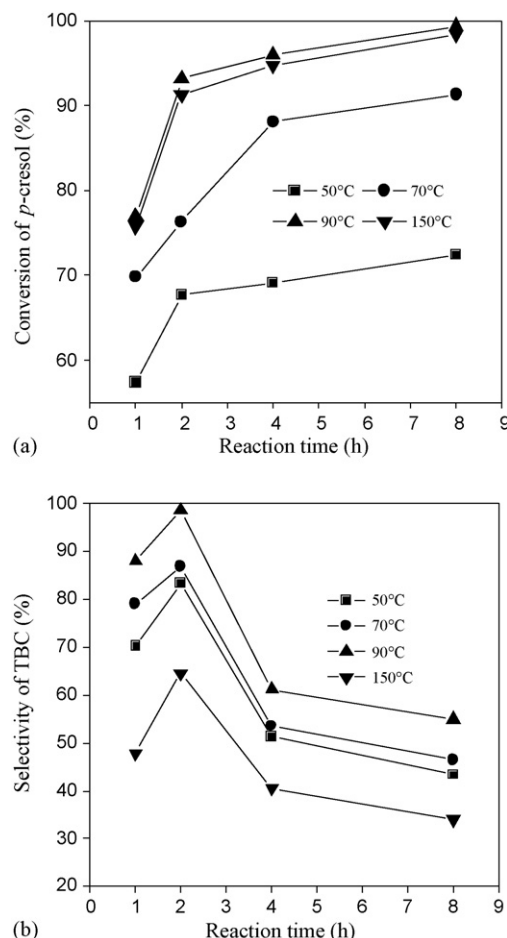

Fig. 1. Effect of reaction time on: (a) conversion of *p*-cresol (%) and (b) selectivity of TBC (%) at different temperature over Zn–Al-MCM-41(75).

strong acidity achieved by several researchers, were found to be less active in the reaction. The small pore size of H-mordenite (7.1 Å) and H-ZSM-5 (5.4 Å) imposes diffusion control through which the bulky product TBC cannot diffuse out with the formation of the small amount of the product probably through a surface reaction (Table 3). It is observed that mesoporous Zn–Al-MCM-41(75) and Zn–Al-MCM-41(151) show high catalytic activity and selectivity for the formation of TBC with no diffusional constraint, while, the selectivity of TBC in Zn–Al-MCM-41(75) is higher than that of other Zn–Al-MCM-41 (Table 3) due to the higher number of Bronsted acid sites on the surface of pore walls caused by the increasing amount of Zn-ions [11]. A slightly decrease in *p*-cresol conversion and TBC selectivity in Al-MCM-41(21) is observed because it has less Bronsted acid strength on the surface pore walls (Table 1). Hence, it can be inferred that the non-framework aluminium-ions existing in the intra-channel space probably increased the catalytic activity by the increased Lewis acidity [28]. Although the pore size and acid strength of the catalyst plays a major role during the synthesis of TBC, which is a large molecule, however the important relationship is between the pore size and molecular size of the reactant/product. The pore size of the catalyst must be accessible to the reactant and

Table 3
t-Butylation of *p*-cresol over various types of catalysts[a]

Catalysts	Si/Zn	Si/Al	*p*-Cresol conversion (%)	TBC selectivity (%)	After reaction[b]	
					Si/Zn	Si/Al
Zn–Al-MCM-41(75)	34	41	93.2	98.60	34.01	41.03
Zn–Al-MCM-41(151)	69	82	87.0	92.87	69.02	82.05
Zn–Al-MCM-41(228)	103	125	80.8	90.09	103.01	125.04
Zn–Al-MCM-41(308)	137	171	73.6	86.54	137.03	171.06
Zn–Al-MCM-41(380)	172	208	65.7	80.06	172.05	208.09
Al-MCM-41(21)	–	21	88.2	90.40	–	21.03
HY (2.6)	–	2.6	25.3	80.40	–	2.63
Hβ (20)	–	20	30.4	74.50	–	20.01
H-mordenite (20)	–	20	23.2	37.30	–	20.02
H-ZSM-5(15)	–	15	10.2	24.30	–	15.03
Recycling 1[c]	–	–	93.4	98.70	34.01	41.03
Recycling 2[c]	–	–	93.3	98.70	34.00	41.02
Recycling 3[c]	–	–	93.5	98.80	34.01	41.03
Recycling 4[c]	–	–	93.6	98.70	34.00	41.01
Recycling 1[d]	–	–	88.2	90.41	–	21.03
Recycling 2[d]	–	–	88.1	90.40	–	21.02
Recycling 3[d]	–	–	88.2	90.39	–	21.03
Recycling 4[d]	–	–	88.2	90.38	–	21.04
Absence of catalyst	–	–	–	–	–	–

[a] Reaction conditions: 0.2 g of catalyst; reaction temperature, 90 °C; reaction time, 2 h; 2:1 mole ratio of *t*-BuOH (32.6 g) to *p*-cresol (24.31 g).
[b] Results obtained from ICP-AES.
[c] Recycling of Zn–Al-MCM-41(75).
[d] Recycling of Al-MCM-41(21) after exhaustive washing with acetone at 40 °C and drying at 200 °C overnight in air.

product molecules in order to take part in the reaction. Thus, the effect of temperature, time, reactant ratios and recylability has also investigated on Zn–Al-MCM-41(75).

3.4. Effect of reaction time and temperature

Fig. 1 shows the result of *t*-butylation of *p*-cresol with 2:1 mole ratio of *t*-BuOH to *p*-cresol at different reaction times and temperatures in the presence of Zn–Al-MCM-41(75). An increase in the conversion of *p*-cresol and selectivity of TBC from 50 to 150 °C for 2 h is observed, but, a decrease in the selectivity for the same reaction temperature with increasing reaction time (>2 h) is observed. Moreover, the selectivity of TBC decreases with increasing the number of byproduct selectivity such as diisobutylene (12.5–25.3%), triisobutylene (7.27–10.33%) and DTBC (25.3–30.4%) when the reaction time (>4 h) and temperature (>90 °C) is further increased. Based on the catalytic results, it is interestingly note that the highest conversion and TBC selectivity are at 90 °C for 2 h. Because the optimal conditions is might be suitable with catalytic activity of the catalyst.

3.5. Effect of t-BuOH to p-cresol ratio

Fig. 2 shows the result of *t*-butylation of *p*-cresol at 90 °C over Zn–Al-MCM-41(75) at different reaction times and mole ratios of *t*-BuOH to *p*-cresol. Generally, the conversion of *p*-cresol increases when the reaction time is increased from 1 to 8 h. An increase in selectivity of TBC up to 2 h is observed, but, the selectivity decreases in the following order of *t*-BuOH to *p*-cresol ratios: 4:1 < 1:1 < 2:1 when the time
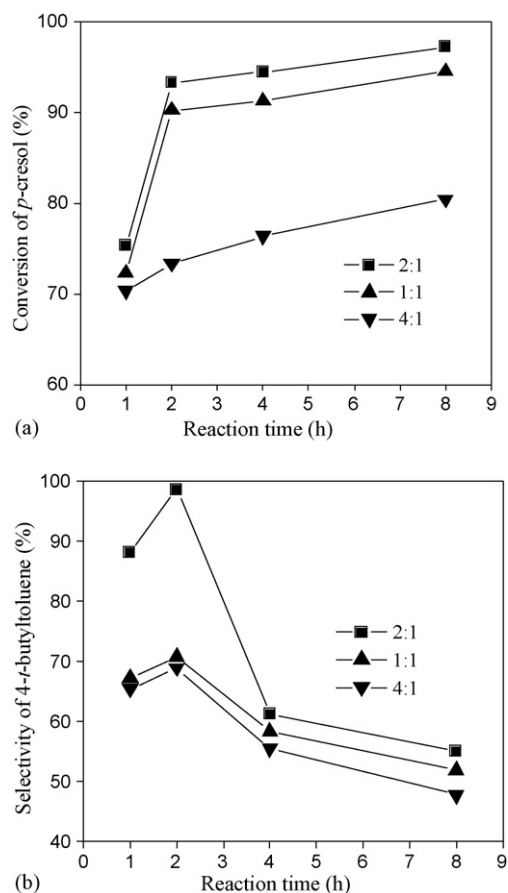

(a)

(b)

Fig. 2. Effect of reaction time on: (a) conversion of *p*-cresol (%) and (b) selectivity of TBC (%) on different mole ratios (*t*-BuOH/*p*-cresol) over Zn–Al-MCM-41(75).

(>2 h) is further increased, because, the number of byproduct selectivity (diisobutylene (7.5–12.5%) and triisobutylene (4.24–7.27%) and DTBC (25.3–40.5%)) increases. Based on the above results, here, it is also interestingly note that the conversion and TBC selectivity in 2:1 mole ratio for 2 h are the highest possibly due to the equilibrium of the reactants with the greater chemisorption on the Bronsted acid sites of catalyst surfaces.

3.6. Recyclability

The Zn–Al-MCM-41(75) and Al-MCM-41(21) catalysts were reused for the *t*-butylation of *p*-cresol at 90 °C for 2 h under 2:1 mole ratio of *t*-BuOH to *p*-cresol for the selective synthesis of TBC; the results have been depicted in Table 3. In these catalytic reactions, no loss of catalytic activity and metal-ions (it has been verified by ICP-AES) on the inner side surface of pore walls in both Zn–Al-MCM-41(75) and Al-MCM-41(21) are observed after four recycles, and their conversion and TBC selectivity remain constant with each cycle. In comparison, the conversion and TBC selectivity in Zn–Al-MCM-41(75) are higher than that of Al-MCM-41(21) due to the higher number of acid sites. The reaction is then performed in the absence of catalyst, and the results have also verified that it did not occur in the absence of catalyst (Table 3).

4. Conclusions

The present study shows that Zn–Al-MCM-41(75) is a relatively strong mild solid acid catalyst, and is a highly active and recyclable catalyst for the green syntheisis of TBC by *t*-butylation of *p*-cresol under mild reaction conditions. Furthermore, the TBC selectivity over Zn–Al-MCM-41(75) is higher than other Zn–Al-MCM-41, Al-MCM-41, HY, Hβ, H-mordenite and H-ZSM-5 due to the higher number of Bronsted acid sites on the surface pore walls.

Acknowledgment

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