Dalton Transactions

Cite this: Dalton Trans., 2012, 41, 14197



Selective synthesis of 6,8-di-*t*-butylated flavan over Zn–Al containing mesoporous silica catalysts[†]

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Received 29th June 2012, Accepted 28th August 2012 DOI: 10.1039/c2dt31409f

Downloaded by Brown University on 17 November 2012 Published on 09 October 2012 on http://pubs.rsc.org | doi:10.1039/C2DT31409F

We demonstrate a much green synthesis method for highly selective synthesis of 6,8-di-*t*-butylated flavan (6,8-DTBF) by liquid phase alkylation of 2,4-di-*t*-butylphenol (2,4-DTBP) with cinnamyl alcohol (Cin-OH) over mesoporous Zn–Al–MCM-41 catalysts synthesized under direct basic hydrothermal method. The main alkylated product, 6,8-DTBF is importantly used as an intermediate in the manufacture of biosynthetic organic compounds. The recyclable mesoporous Zn–Al–MCM-41 catalysts have also been reused in this reaction to study their catalytic activities. The influences of various reaction parameters such as temperature, time, ratios of reactant (2,4-DTBP-to-Cin-OH) have been extensively investigated for the synthesis of 6,8-DTBF. In addition, dimethyl sulfoxide (DMSO) has also been used as a solvent in this catalytic reaction. The mesoporous Zn–Al–MCM-41(75) gives excellent catalytic activity with 6,8-DTBF selectivity (86.0%) and 2,4-DTBP conversion (63.1%), and these catalytic results have also compared with that obtained using other mesoporous and microporous catalysts. On the basis of catalytic activity obtained by using the all catalysts, the Zn–Al–MCM-41(75) catalyst is found to be a highly active, recyclable and eco-friendly heterogeneous catalyst in the liquid-phase alkylation of 2,4-DTBP.

1. Introduction

Friedel-Crafts alkylation is an important reaction for attaching alkyl chains to aromatic rings. The alkylation is traditionally performed, with alkyl halides or alcohols as the alkylating regents using Lewis acid catalysts such as AlCl₃, FeCl₃ and ZnCl₂.¹ However, the separation of homogeneous catalysts is not easy after the reaction, and that catalytic system causes large amounts of acid wastes. The use of homogeneous catalysts gives rise to many problems such as a high corrosiveness, tedious work-up, requirement of stoichiometric quantities, several undesirable side products. The homogeneous catalysts cannot be reused and thus are highly non-ecofriendly. The major goals of 'green chemistry' are to increase the product selectivity, to maximize the use of starting materials, and to replace hazardous and stoichiometric reagents with eco-friendly catalysts in order to facilitate an easy separation of the final reaction mixture, including recovery of the catalyst, and also reusable. Active research has been addressed for substituting the traditional homogeneous catalysts

by heterogeneous solid acid ones, such as clay minerals and zeolites. Therefore, some solid acid catalysts are used in the alkylation of aromatics. Particularly, microporous zeolites are used in the alkylation of 2,4-DTBP with Cin-OH, however, they give a less yield of flavan (<10%) because of their small pore sizes that are unsuitable in this catalytic reaction.² The microporous zeolites produce several byproducts with flavan product, and complicated and expensive processes might be needed to separate the flavan products.²

Recently, the green catalytic reaction processes have been importantly focusing with minimal environmental threats and maximal economical benefits. A great demand in fine chemical industries begins to develop a suitable heterogeneous catalyst with a large number of Brønsted acid sites for mild reaction conditions without employing toxic materials. In 1992, the highly ordered mesoporous silicate materials discovered with high surface area, large pore size, and large pore volume have attracted a great interest for their catalytic applications.³ Although the mesoporous MCM-41 materials offer great advantages for the conversion of bulky molecules in the studies of catalysis, pure mesoporous silica materials have not been used as catalysts or catalyst supports in industry yet due to the lack of acidity and poor hydrothermal stability. Furthermore, these mesoporous materials are easily destroyed in boiling water and steam as a result of the fast hydrolysis of the relatively thin amorphous silica pore walls.⁴ Thus, huge amounts of Al-ions into the mesoporous silica walls are incorporated to improve the surface acidity and hydrothermal stabilities.^{5–7} Generally, mesoporous Al-MCM-41 materials have lower content of acid sites as compared to zeolites. Because of its uniformly hexagonal pore size,

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[†]Electronic supplementary information (ESI) available. See DOI: 10.1039/c2dt31409f

mesoporous Al–MCM-41 is a promising catalyst in the production of bulky fine chemicals like 6,8-DTBF.² Al-incorporated into HMS, ethane- and benzene-mesoporous silicas have also been used for the synthesis of 6,8-DTBF, and the catalysts are produced up to 75% selectivity of 6,8-DTBF.^{2,8–10} Additionally, various mesoporous catalysts have also been used in alkylation of aromatics.^{11–14}

Selvaraj and his research group have reported the details of the synthesis and characterization of mesoporous Zn–Al– MCM-41 catalysts which have been used as the alkylation catalysts for the synthesis of fine chemicals along with 'a goal of green chemistry'.^{15–19} To the best of our knowledge, the mesoporous Zn–Al–MCM-41 molecular sieves have not been used as the green catalysts for the synthesis of 6,8-DTBF. Herein we disclose the report of selective synthesis of 6,8-DTBF using Zn– Al–MCM-41 catalysts under mild reaction conditions. The catalytic results of Zn–Al–MCM-41, for the selective synthesis of 6,8-DTBF, have also been correlated and compared with other solid catalysts, such as Al–MCM-41(21), Zn–MCM-41(21), USY, H β , H-ZSM-5 and H-mordenite, including a strong acid catalyst, 1 N H₂SO₄.

2. Experimental

The diverse mesoporous catalysts, such as MCM-41, Zn–Al– MCM-41 catalysts $(n_{Si}/(n_{Zn} + n_{Al}) = 75, 151, 228, 304$ and 380), Al–MCM-41 $(n_{Si}/n_{Al} = 21)$ and Zn–MCM-41 $(n_{Si}/n_{Zn} = 21)$, were synthesized under direct hydrothermal method and characterized according to our previous published procedure. ^{15,16,20,21} H β $(n_{Si}/n_{Al} = 20, Strem)$; 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. For the removal of moisture from the inner surface of pores, these catalysts were then calcined at 200 °C in air for 6 h before catalytic reaction. 1 N H₂SO₄ was also used as an acid catalyst in this catalytic reaction.

The alkylation of 2,4-DTBP (Aldrich) with Cin-OH (Aldrich) was carried out under vigorous stirring in a thermostated glass vessel reactor. In a typical experimental procedure, 1.0 mmol 2,4-DTBP (206 mg), 1.0 mmol Cin-OH (134 mg) and 50.0 mL isooctane as a solvent were taken in the glass vessel reactor. The reaction mixture was stirred under constant stirring, and subsequently the reaction temperature was slowly raised to 363 K and then 200 mg of Zn-Al-MCM-41(75) catalyst was added. After a reaction time of 24 h as well as reaching the reactor temperature to room temperature, the catalyst was filtered and extracted with dichloromethane to recover the adsorbed reaction products. The alkylation of 2,4-DTBP was also carried under the same reaction conditions using a variety of mesoporous and microporous catalysts, and an acid catalyst, 1 N H₂SO₄. To find an optimal condition over Zn-Al-MCM-41(75), the catalytic reaction was further carried out with different reaction conditions such as time, temperature, stoichiometric molar ratios of reactants (2,4-DTBP-to-Cin-OH). Additionally, this reaction was also carried out with DMSO solvent.

The collected products were analyzed with authentic samples using an Agilent 6890 gas chromatograph equipped with a flame ionization detector (FID) and an OV-1 capillary column ($30 \text{ m} \times$

 $0.25 \text{ mm} \times 0.3 \text{ }\mu\text{m}$). Additionally, the products were further confirmed using gas chromatography combined mass spectroscopy (GC-MS). 1,3-Di-*t*-butylbenzene and toluene were used as an internal standard for the quantitative analysis of the products.

The high and low metal content containing mesoporous catalysts, such as Zn-Al-MCM-41(75) and Zn-Al-MCM-41(380), respectively, were reused in the alkylation of 2,4-DTBP to study their catalytic stabilities. In a typical experimental procedure, the Zn-Al-MCM-41(75) catalyst used in a catalytic run was separated from the reaction mixture, washed with dichloromethane several times and dried at 393 K. Finally, the Zn-Al-MCM-41-(75) catalyst was calcined at 473 K for 6 h in air to remove the adsorbed species (like products and unreacted reactants) and again reused for further catalytic runs. The recyclable Zn-Al-MCM-41(75) has been regenerated before applying to each run. A similar procedure was used for recycling studies of other catalysts like Zn-Al-MCM-41(380). After completion of the reaction, the catalyst was filtered and analyzed by ICP-AES to determine the percentage of Zn and Al, and the conversion of 2,4-DTBP and selectivity of 6,8-DTBF were calculated with the standard formulas obtained by analyzing the results of GC and GC-MS.

3. Results and discussion

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

The diverse mesoporous catalysts, such as Zn-Al-MCM-41(75), Zn-Al-MCM-41(151), Zn-Al-MCM-41(228), Zn-Al-MCM-41(304) and Zn-Al-MCM-41(380), Al-MCM-41(21), Zn-MCM-41(21) and MCM-41, synthesized by direct hydrothermal method, have been characterized using the relevant instrumental techniques according to the published method.^{15,16,20,21} Based on the physico-chemical characterization results, it can be observed from the XRD patterns (Fig. 1S⁺) of a variety of mesoporous catalysts, such as Zn-Al-MCM-41, Al-MCM-41(21) and Zn-MCM-41(21) that the structural properties, such as d-spacing value (d_{100}) and unit cell parameter (a_0) , decrease with increasing the metal-ions content (Table 1). FT-IR studies, as shown in Fig. 2S,† predict that zinc- and aluminum-ions are incorporated into the hexagonal mesoporous MCM-41 materials; the infrared wavenumber of the antisymmetric Si-O-Si vibration bands (1096 cm⁻¹) in Zn-Al-MCM 41 is higher than that of Al-MCM-41 and Zn-MCM-41 (1083 or 1085 cm⁻¹), and this shift should be attributed to the increase of the mean Si-O distance in the surface wall caused by the incorporation of the small ionic radii of silicon by the larger ionic radii of zinc.¹⁶ The zincand aluminum-ions content on the silica surface, before and after catalytic reaction of 2,4-DTBP, have been determined by ICP-AES (Table 1). The textural properties, such as 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 (Table 1), but the total and Brønsted-Lewis acid sites in Zn-Al-MCM-41(75), as shown in Table 1S[†] and Fig. 3S,[†] are higher than that in other Zn-Al-MCM-41, Al-MCM-41(21) and Zn-MCM-41(21) due to increasing the number of acid sites by the introduction of zinc ions.¹⁶ SEM studies confirm that the all calcined Zn-Al-MCM-41 catalysts have either micellar rod-like

Table 1 Physico-chemical properties of Zn-Al-MCM-41 catalysts prepared by basic hydrothermal method

Catalysts	Zn content ^{a} (wt%)	Al content ^{a} (wt%)	$d_{100}({\rm \AA})$	a_0 (Å)	$SA_{\rm BET} (m^2 g^{-1})$	$D_{\rm p}({\rm \AA})$	$V_{\rm p} ({\rm cm}^3~{\rm g}^{-1})$	$t_{\rm w}({\rm \AA})$
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	15.24
$Zn-Al-MCM-41(75)^{6}$	0.122	0.219	37.85	43.70	810	22.9	0.852	20.80
$Zn-Al-MCM-41(380)^{b}$	0.020	0.049	41.00	46.32	1018	31.5	0.982	14.82
Al-MCM-41(21)		0.499	38.41	44.35	830	27.5	0.866	16.85
Zn-MCM-41(21)	0.242		37.9	43.76	635	27.3	0.611	16.46
MCM-41	—	—	35.90	41.45	1179	29.3	0.675	12.15
^{<i>a</i>} The results were obtaine	d by ICP-AES. ^b The r	esults were obtained for	or the recycla	ble catalys	ts used in 4th run.			

hexagonal shape or spherical edge (Fig. 4S†).¹⁶ The uniform pore channels with its hexagonal symmetry can be clearly identified by the TEM images of Zn–Al–MCM-41(75), indicating that the all mesoporous Zn–Al–MCM-41 catalysts synthesized under basic hydrothermal method have uniform mesostructures (Fig. 5S†) as inferred by the XRD results.¹⁶

3.2. Alkylation of 2,4-di-t-butylphenol with cinnamyl alcohol

The liquid phase alkylation of 2,4-DTBP has been conducted over mesoporous and microporous solid catalysts with 1:1 mmol ratio of 2,4-DTBP to Cin-OH at 363 K for 24 h, as shown in Scheme 1. In this alkylation reaction 6,8-di-*t*-butyl-2phenyl-2,3-dihydro[4*H*]benzopyran or 6,8-di-*t*-butylated flavan (6,8-DTBF, Product 1) forms as a major product by an intramolecular cyclization of the primary cinnamyl phenol intermediate (Product 4). Additionally, the 4-*t*-butylphenol (4-TBP, Product 2) as a primary byproduct produces by acid catalyzed dealkylation



Scheme 1 Reaction products obtained by alkylation of 2,4-DTBP with Cin-OH over Zn–Al–MCM-41 catalysts.

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of 2,4-DTBP, and subsequently 6-*t*-Butyl-2-phenyl-2,3-dihydro-[4*H*]benzopyran or 6-*t*-butylated flavan (6-TBF, Product 3) also forms as a secondary byproduct by the dealkyation of 6,8-DTBF or alkylation of 4-TBP with Cin-OH.

3.3. Selectivity of 6,8-di-t-butylated flavan

The alkylation of 2,4-DTBP with Cin-OH (Scheme 1) for the highly selective synthesis of 6,8-DTBF was carried out by using the reaction conditions noted in Table 2 over mesoporous and microporous solid acid catalysts.

In 1995, Armengol et al. applied the mesoporous aluminosilicate MCM-41 as a convenient solid acid catalyst in the liquid phase alkylation of 2,4-DTBP with Cin-OH, and that catalyst is produced 35% of 6,8-DTBF yield with 25% of 4-TBP yield as a main byproduct.² Pauly *et al.* reported that in the similar catalytic system the 6,8-DTBF selectivity is 71.8% and 74.2% over Al-MCM-41 and Al-HMS, respectively.⁸ Aluminum-containing mesoporous ethane- and benzene-silicas produce 25.3-27.5% of 6,8-DTBF selectivity with 51.3% of 4-TBP selectivity.9,10 From the above literature results, we found that monometallic mesoporous silicas are produced up to 75% selectivity of 6,8-DTBF due to increasing the selectivity of dealkylated products whereas aluminum containing organosilicas lead two times less selectivity of 6,8-DTBF as compared to the selectivity of primary cinnamylphenol. To improve the selectivity of 6,8-DTBF, the mesoporous Zn-Al-MCM-41 catalysts have been used in this catalytic reaction. In order to increase the conversion of 2,4-DTBP as in the series of the catalysts: Zn-Al-MCM-41(75) >Zn-Al-MCM-41(151) > Al-MCM-41(21) > Zn-Al-MCM-41-(228) > Zn-MCM-41(21) > Zn-Al-MCM-41(304) > Zn-Al- $MCM-41(380) > 1 N H_2SO_4 > H\beta(20) > HY(2.6) > H-morde$ nite(20) \geq H-ZSM-5(15). It has been observed that the mesoporous Zn-Al-MCM-41(75) shows that its high catalytic activity has been enhanced in the production of 6,8-DTBF with no diffusional constraint, as 2,4-DTBP conversion (63.1%) and 6,8-DTBF selectivity (86.0%) in Zn-Al-MCM-41(75) are higher than that of other Zn-Al-MCM-41 (Table 2) due to the higher number of Brønsted acid sites on the surface of pore walls caused by the increasing amounts of Zn-ions.^{15,16} Additionally, Zn-Al-MCM-41(75) produces higher selectivity of 6,8-DTBF than Al-MCM-41, as found in the literatures, due to promotion of the catalytic activity, which was caused by the introduction of high Zn-ions on the surface of Al-MCM-41.15,16 4-TBP

Catalysts			Selectivity (%)			
	Conversion of 2,4-DTBP (%)	Yield of 6,8-DTBF (%)	1	2	3	4
Zn-Al-MCM-41(75)	63.1	54.3	86.0	12.6	1.4	
Zn-Al-MCM-41(151)	52.2	39.2	75.2	10.1	1.1	13.6
Zn-Al-MCM-41(228)	43.4	27.4	63.3	8.3	1.0	27.4
Zn-Al-MCM-41(304)	34.2	17.8	52.1	6.7	1.0	40.2
Zn-Al-MCM-41(380)	25.3	10.7	42.3	5.8	1.0	50.9
HY (2.6)	7.5	6.1	82.0	6.2		11.8
Ηβ (20)	9.5	8.1	85.5	7.7		6.8
H-mordenite (20)	5.4	4.0	73.5	5.0		21.5
HZSM-5(15)	4.8	3.6	77.0	5.0		18.0
$1 \text{ N H}_2 SO_4^{b'}$	21.3	9.1	43.0	35.2	18.2	3.6^{c}
$Zn-Al-MCM-41(75)^d$	62.9	53.9	85.8	12.4	1.8	
$Zn-Al-MCM-41(75)^{e}$	61.8	45.2	73.2	12.5	14.3	
Al-MCM-41(21)	49.3	36.7	74.4	9.8	1.1	14.7
Zn-MCM-41(21)	40.1	12.2	30.5	47.5	22.0	
MCM-41	5.0	<1	2			98 ^g
Filtrate solution ^f	10	<1	5	7	8	80^g

 Table 2
 Alkylation of 2,4-DTBP with Cin-OH over various types of catalysts^a

^{*a*} Reaction conditions: 200 mg of catalyst, 1 : 1 mmol ratio of 2,4-DTBP to Cin-OH, 50 ml of isooctane, T = 363 K, t = 24 h. ^{*b*} 50 mg. ^{*c*} Tri-*t*-butylphenol. ^{*d*} Dimethyl sulfoxide was used as a solvent. ^{*e*} Dimethyl sulfoxide was used at 383 K. ^{*f*} The results obtained from the hot-filtrate solution after Zn–Al–MCM-41(75) catalyst removal. ^{*g*} Unreacted reactants.

selectivity in Zn-Al-MCM-41(75) is also higher than that of other Zn-Al-MCM-41. Al-MCM-41(21) catalyst has produced higher 6.8-DTBF selectivity than Zn-MCM-41(21) due to increasing Brønsted acid sites on the surface of pore walls whereas the Zn-MCM-41(21) leads to increase the dealkylated products due to acting Lewis solid acid catalyst, as shown in the literature.²² Based on the literature results, it can be observed from the results of FT-IR-pyridine and ammonia-TPD that the acid sites of the all microporous catalysts are almost similar except H-ZSM-5.²³ Zeolite Hβ (pore size, 7.6 and 5.4 Å), which has a 9.5% 2,4-DTBP conversion, is found to be more active than HY (pore size, 7.4 Å), which has a 7.5% 2,4-DTBP conversion. These catalytic results clearly show that both catalysts (HB and HY) cannot be allowed the bulky reactants, 2,4-DTBP and Cin-OH, to enter into their pore sizes. 2,4-DTBP conversion in HY and H β is less than 10% due to less acid sites on their external surfaces but their inner pore sizes have strong acid sites, which could not help for this catalytic reaction.² Although 2,4-DTBP conversion is less, 6,8-DTBF selectivity in both catalysts is high, as the 6,8-DTBF selectivity (85.5%) in H β is higher than that (82%) of HY. It can be also observed from the catalytic results that the higher selectivity of HB might be attributed to its outer surface acid sites, and hence a higher selectivity of 6,8-DTBF is achieved over H
ß rather than HY zeolite. In contrast, some microporous zeolites (H-mordenite and H-ZSM-5) were also found to be much less active in the reaction. The 2,4-DTBP molecule is too large to enter the pores of ZSM-5 (5.4 Å) and H-mordenite (7.1 Å). Hence, the reaction should proceed only on the outer surfaces of ZSM-5 and H-mordenite. Although the reaction is suggested to be catalyzed by moderately acidic sites, ZSM-5 gives slightly higher 6,8-DTBF selectivity than H-mordenite, as shown in Table 2. It might be also attributed to the stronger acidic strength on ZSM-5. However, 2,4-DTBP conversion in ZSM-5 is much less than that of H-mordenite, as shown in Table 2. In all microporous catalysts the 6-TBF selectivity is also much less than 8%. On the basis of the catalytic results, it

has been observed that the microporous catalysts are unsuitable for the higher conversion of 2,4-DTBP by the alkylation of 2,4-DTBP with Cin-OH.

An acid catalyst, 1 N H₂SO₄ has been used in this catalytic reaction and gives 2,4-DTBP conversion (21.3%) with a 6,8-DTBF selectivity (43%) which is much less as compared to solid acid mesoporous catalyst, Zn-Al-MCM-41(75), but the 1 N H_2SO_4 gives 4-TBP selectivity (35.2%), which is higher as compared to other solid catalysts used in this reaction due to its strong acidity (Table 2). DMSO has been used as a solvent in this catalytic reaction under the same reaction condition over Zn-Al-MCM-41(75) and gives 2,4-DTBP conversion (62.9%) with 6,8-DTBF selectivity (85.8%), and its catalytic activity is almost similar to isooctane solvent used as solvent in this catalytic reaction (Table 2). The 6,8-DTBF selectivity (Table 2) decreases when this catalytic reaction is carried out in the presence of DMSO at 383 K because of the increase of the byproducts selectivity, 4-TBP (12.5%) and 6-TBF (14.3%), as reported by Armengol et al.² On the basis of the literatures, it can be also observed that the catalytic activity of Zn-Al-MCM-41(75) is higher as compared to other catalysts used for this catalytic reaction.^{2,8-10} On the basis of the performance of the catalytic activity over different Zn-Al-MCM-41 mesoporous catalysts, the well hexagonally ordered Zn-Al-MCM-41(75) is found to be a promising heterogeneous catalyst in the liquidphase alkylation of 2,4-DTBP for the highly selective synthesis of 6,8-DTBF. In conclusion it can be also confirmed that the well ordered mesoporosity with huge amounts of Zn and Al loadings plays an important catalytic role in the production of 6,8-DTBF with a higher selectivity.

3.4. Effect of reaction temperature and time

Fig. 1 and 2 show the results of alkylation of 2,4-DTBP with 1:1 mmol ratio of 2,4-DTBP to Cin-OH at different reaction



Fig. 1 Effect of reaction temperature over Zn–Al–MCM-41(75). *Reaction conditions*: 200 mg of catalyst, 1:1 mmol ratio of 2,4-DTBP to Cin-OH, 50 ml of isooctane and t = 24 h.



Fig. 2 Effect of reaction time over Zn–Al–MCM-41(75). *Reaction conditions*: 200 mg of catalyst, 1:1 mmol ratio of 2,4-DTBP to Cin-OH, 50 ml of isooctane and T = 363 K.

times and temperatures over Zn-Al-MCM-41(75). With increasing temperature from 333 to 363 K for 24 h, 2,4-DTBP conversion as well as 6.8-DTBF selectivity gradually increases, and byproduct selectivity (4-TBP) also slightly increases by the acid catalyzed dealkylation of 2,4-DTBP. Moreover, 2,4-DTBP conversion as well as 6,8-DTBF selectivity increases with increasing time from 6 to 24 h whereas the conversion and selectivity decrease at 48 h due to increasing of the byproduct selectivity (4-TBP and 6-TBF) by the acid catalyzed dealkylation of 2,4-DTBP or 6,8-DTBF at a longer time.² At low reaction temperature (<343 K) as well as reaction time (<12 h), the formation of primary cinnamyl phenol increases due to the less chemisorption occurred between the reactants and the Brønsted acid sites of catalytic surface. Based on the catalytic results, it is interesting to note that the reaction temperature (363 K) and time (24 h) are suitable to be a better conversion of 2,4-DTBP as well as selectivity of 6,8-DTBF while the active sites of Zn-Al-MCM-41-



Fig. 3 Effect of 2,4-DTBP to Cin-OH ratios over Zn–Al–MCM-41-(75). *Reaction conditions*: 200 mg of catalyst, 50 ml of isooctane, T = 363 K and t = 24 h.

(75) at 363 K for 48 h have not been changed that can be measured by the studies of remarkably hydrothermal stability and acidity measurements.¹⁶

3.5. Effect of 2,4-di-t-butylphenol to cinnamyl alcohol ratio

To find the best ratio of 2.4-DTBP to Cin-OH for the highly selective synthesis of 6,8-DTBF, the liquid phase alkylation of 2,4-DTBP has been carried out with different ratios of $n_{2,4-\text{DTBP}}$ $n_{\text{Cin-OH}}$ at 363 K for 24 h over Zn–Al–MCM-41(75) as shown in Fig. 3. When this reaction is carried out with 1:1 mmol ratio, 2,4-DTBP conversion (63.1%) as well as 6,8-DTBF selectivity (86.0%) can be observed because of the equilibrium of the reactants with the greater chemisorption on the Brønsted acid sites of catalyst surfaces. The decrease in 6,8-DTBF selectivity is observed in other mmol ratios of 1:2 and 2:1 because of increasing of the byproducts selectivity. Particularly, 4-TBP selectivity (15.5%) in the ratio of 2:1 as well as a primary cinnamylphenol (17.6%) in the ratio of 1:2 can be observed. It is clearly found a correct reason in the decrease of 6,8-DTBF selectivity, as the formation of byproducts increase by using unevenly ratios of reactants whereas the surface acid sites of catalyst in the ratio of 1:2 may be deactivated due to the formation of polymerized products of cinnamyl alcohol.² On the basis of the effect of the ratios, it can be clearly noted that 1:1 mmol ratio of 2,4-DTBP to Cin-OH is an optimum ratio for the highly selective synthesis of 6,8-DTBF.

3.6. Recyclability

The bimetallic mesoporous catalysts, Zn–Al–MCM-41(75) and Zn–Al–MCM-41(380), have been examined to determine their catalytic stabilities as follows. Initially, these catalysts used in the catalytic reaction usually suffer from the loss of catalytic activities, and hence the catalysts need to be regenerated by chemical treatments and calcination. At first the recycled catalysts were washed several times with dichloromethane and dried





Fig. 4 Effects of recyclability ((a) conversion and (b) yield and selectivity) over various mesoporous solid catalysts. *Reaction conditions*: 200 mg of catalyst, 1 : 1 mmol ratio of 2,4-DTBP to Cin-OH, 50 ml of isooctane, t = 24 h and T = 363 K.

at 393 K overnight. Further, the catalysts were calcined at 473 K for 6 h in air for complete removal of the organics and unreacted 2,4-DTBP molecules. The treated catalysts have been reused as recyclable catalyst in this reaction, as shown in Fig. 4. Using the above procedure, the recyclable catalyst has been regenerated before applying to each run. The 2,4-DTBP conversion as well as 6,8-DTBF selectivity slightly increase in the first two runs (Fig. 4). On the basis of first and second runs, it can be clearly observed that somewhat active sites on the inner pore surface of Zn-Al-MCM-41(75) have been blocked by the non-framework octahedral aluminum and zinc oxides that are completely removed after washing with dichloromethane. After third and fourth runs, the 2,4-DTBP conversion as well as 6,8-DTBF selectivity remains constant, indicating that the incorporated or substituted active species could not be leached on the mesoporous silica matrix, which is in good agreement with ICP-AES results of Zn-Al-MCM-41(75) obtained after the recyclable

reactions, as shown in Table 1. The conversion and selectivity in Zn-Al-MCM-41(380) almost remain constant with each cycle because the low active species can be homogeneously incorporated on the inner silica pore walls, as a better catalytic activity found in Zn-Al-MCM-41(380). The metal-ions in Zn-Al-MCM-41(380) have also been measured by ICP-ACS after the recyclable reaction (Table 1). After collecting the results of four runs over Zn-Al-MCM-41(75), the results of hot-catalyst filtration experiments were also carried out twice at 363 K during alkylation of 2,4-DTBP with Cin-OH. In this case, the filtrate solution gives a very low 2,4-DTBP conversion (10%) with trace amount of 6,8-DTBF yield, indicating that the alkylation of 2,4-DTBP takes place on the surface of Zn-Al-MCM-41(75) and is found as a true heterogeneous process.^{24,25} This reaction was also carried out using pure MCM-41 synthesized by basic hydrothermal method.²⁰ In this case, conversion of 2,4-DTBP (5%) forms with a trace amount of 6,8-DTBF selectivity (Table 2), thus indicating that major activity is only due to both metal-ions, Al- and Zn-ions, incorporated in the framework of MCM-41.

4. Conclusions

The bimetallic mesoporous Zn–Al–MCM-41 catalysts have been successfully used for the synthesis of 6,8-DTBF. The active sites of these catalysts are highly efficient for the generation and intramolecular cyclization of cinnamylphenol intermediate to 6,8-DTBF. Zn–Al–MCM-41(75) has higher catalytic activity in the liquid-phase alkylation of 2,4-DTBP as compared to other mesoporous and microporous catalysts, and an acid catalyst, 1 N H₂SO₄, due to the higher number of Brønsted acid sites on the surface pore walls. From the optimized conditions, it can be found that the higher 6,8-DTBF selectivity and 2,4-DTBP conversion are obtained at 363 K for 24 h using 1 : 1 mmol ratio of 2,4-DTBP to Cin-OH with 50 ml isooctane. On the basis of all catalytic studies, it is clearly found that the Zn–Al–MCM-41(75) catalyst is a highly active, recyclable and promising heterogeneous catalyst for the selective synthesis of 6,8-DTBF.

Acknowledgements

This research work was supported by Basic Science Research Program through the National Research Foundation (NRF) of Korea funded by the Ministry of Education, Science and Technology (2012-0007172).

References

- Ullmann's Encyclopedia of Industrial Chemistry, ed. H.-W. Voges, B. Elvers, S. Hawkins and G. Schulz, VCH, Weinheim, 1991, vol. A19, 328.
- 2 E. Armengol, M. L. Cano, A. Corma, H. Garcia and M. T. Navarro, J. Chem. Soc., Chem. Commun., 1995, 519.
- 3 C. T. Kresge, M. E. Leonowicz, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
- 4 P. Van Der Voort, M. Baltes and E. F. Vansant, *Catal. Today*, 2001, 68, 119.
- 5 A. Corma, Chem. Rev., 1997, 97, 2373.
- 6 A. Corma, V. Forance, M. T. Navarro and J. Perez-Parients, J. Catal., 1994, 148, 569.
- 7 M. Selvaraj, A. Pandurangan, K. S. Seshadri, P. K. Sinha, V. Krishnasamy and K. B. Lal, J. Mol. Catal. A: Chem., 2002, 186, 173.

- 8 T. R. Pauly, Y. Liu, T. J. Pinnavaia, S. J. L. Billinge and T. P. Rieker, J. Am. Chem. Soc., 1999, **121**, 8835.
- 9 Q. Yang, Y. Li, L. Zhang, J. Yang, J. Liu and C. Li, J. Phys. Chem. B, 2004, 108, 7934.
- 10 Q. Yang, J. Yang, Z. Feng and Y. Li, J. Mater. Chem., 2005, 15, 4268.
- 11 S. K. Das, M. K. Bhunia, A. K. Sinha and A. Bhaumik, J. Phys. Chem. C, 2009, **113**, 8918.
- 12 P. K. Thallapally, C. A. Fernandez, R. K. Motkuri, S. K. Nune, J. Li and C. H. F. Peden, *Dalton Trans.*, 2010, **39**, 1692.
- 13 M. Fujiwara, A. Sakamoto, K. Shiokawa, A. K. Patra and A. Bhaumik, *Microporous Mesoporous Mater.*, 2011, 142, 381.
- 14 J.-L. Niu, X.-Q. Hao, J.-F. Gong and M.-P. Song, *Dalton Trans.*, 2011, 40, 5135.
- 15 M. Selvaraj, A. Pandurangan, K. S. Seshadri, P. K. Sinha and K. B. Lal, *Appl. Catal.*, A, 2003, 242, 347.
- 16 M. Selvaraj, B. R. Min, Y. G. Shul and T. G. Lee, *Microporous Mesoporous Mater.*, 2004, 74, 143.

- 17 M. Selvaraj and P. K. Sinha, J. Mol. Catal. A: Chem., 2007, 264, 44.
- 18 M. Selvaraj and S. Kawi, J. Mol. Catal. A: Chem., 2007, 265, 250.
- 19 M. Selvaraj and S. Kawi, *Microporous Mesoporous Mater.*, 2008, 109, 458.
- 20 M. Selvaraj, S. W. Song and S. Kawi, *Microporous Mesoporous Mater.*, 2008, **110**, 472.
- 21 M. Selvaraj, PhD thesis, Anna University, Tamil Nadu, India, 2002.
- 22 E. A. Gunnewegh, S. S. Gopie and H. v. Bekkum, J. Mol. Catal. A: Chem., 1996, 106, 151.
- 23 J. Medina-Valtieera, M. A. Sanchez, J. A. Montoya, J. Navarrete and J. A. de los Reyes, *Appl. Catal.*, A, 1997, **158**, L1.
- 24 R. A. Sheldon, M. Wallau, I. W. C. E. Arends and U. Schuchardt, Acc. Chem. Res., 1998, 31, 485.
- 25 J. Dedecek, N. Zilkova and J. Cejka, Microporous Mesoporous Mater., 2001, 44–45, 259.