Journal of Catalysis 290 (2012) 101-107

Contents lists available at SciVerse ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

### Microwave-induced deactivation-free catalytic activity of BEA zeolite in acylation reactions

#### B.M. Chandra Shekara, B.S. Jai Prakash, Y.S. Bhat\*

Department of Chemistry, Bangalore Institute of Technology, KR Road, Bangalore 560 004, India

#### ARTICLE INFO

Article history: Received 25 January 2012 Revised 6 March 2012 Accepted 7 March 2012 Available online 18 April 2012

Keywords: Microwave irradiation BEA Catalyst deactivation Acylation P-cresol

#### ABSTRACT

Solventless liquid-phase acylation of p-cresol with different aliphatic carboxylic acids like acetic, propionic, butyric, hexanoic, octanoic, and decanoic acids was investigated over BEA zeolite under conventional as well as microwave heating. An unanticipated huge difference in activity was observed between two modes of heating. Under conventional heating, conversion of all the acids was less than 20%, while under microwave heating, the conversion was in the range of 50–80%. Ester formed through O-acylation and ortho-hydroxyketone formed through Fries rearrangement of the ester were the only products. Conversion of carboxylic acid increased with chain length up to hexanoic acid and then it showed a decrease in the trend. With all the acids, O-acylation occurred rapidly followed by slow conversion to ortho-hydroxyketone. The ketone/ester ratio increased with catalyst amount, temperature, and reaction time. Used catalyst samples were characterized by TGA, XRD, and IR studies to understand lower activity and deactivation behavior under conventional heating. The results showed absence of coke precursor/coke on the catalyst used in microwave-irradiated reactions in contrast to catalyst used in conventionally heated ones. Higher yield in the case of microwave-assisted reactions is attributed to the prevention of coke precursor/ coke on the active sites by microwaves.

© 2012 Elsevier Inc. All rights reserved.

JOURNAL OF CATALYSIS

#### 1. Introduction

The acylation of phenolic substrates is an important organic reaction in the fine and specialty chemical industries. Direct acylation of hydroxyl group yields ester, which can be converted to ketone by subsequent Fries rearrangement. Both ester and ketone formed in the reaction are valuable intermediates in the synthesis of pharmaceuticals and fragrances [1]. Acylation reactions are generally catalyzed by strong protonic acids and Lewis acids such as AlCl<sub>3</sub> and BF<sub>3</sub>. These catalysts, besides being highly corrosive, are often required to be used in more than stoichiometric amounts. They are difficult to handle, not reusable, and the work-up procedure generates large amounts of polluting wastes [2]. Efforts have been made to replace these acids by reusable, eco-compatible heterogeneous solid acids like zeolites, acidic clays, and heteropoly acids [3]. It is also highly desirable to use less hazardous acylating agents like carboxylic acids instead of acyl halides and anhydrides. Acidic zeolites are the most studied heterogeneous catalysts for the acylation, and in an important development, Rhodia company has established the first industrial-scale application of zeolites for the acylation of anisole and veratrole [4]. BEA zeolite with tunable acidity and three-dimensional large pore accessibility to reacting molecules is a potential solid acid for various organic transformations [5,6]. It has been studied as a catalyst in the acylation and related Fries rearrangement of several organic substrates. Acylation of arenes like toluene, biphenyl, and naphthalene, aromatic ethers like anisole, thioanisole, veratrole, and 2-methoxy naphthalene, heterocyclic compound like thiophene, and phenolic compounds like phenol and resorcinol have been investigated using BEA zeolite as catalyst [7–17]. Major problems faced in the acylation over zeolites are lower conversions and longer reaction times, especially when less-reactive acylating agents like carboxylic acids are used [18]. Main reason for lower rate is the initial inhibition of the reaction due to preferential adsorption of carboxylic acids and deactivation of the catalyst [19]. Acidity, hydrophobicity, and crystallite size of BEA zeolite were found to be the other important factors influencing the conversion and catalyst deactivation [20].

Microwave-assisted organic synthesis has attracted a considerable interest in recent years. Principally, in all type of thermally driven chemical reactions, use of microwave irradiation as a source of heat can profoundly reduce the reaction times [21–23]. Even though there is lot of scope to improve the efficiency of acylation reactions over zeolites under microwave heating, reports of these are scarce in the literature [24,25]. Acylation of phenolic substrates using carboxylic acids over zeolites is one such reaction, where microwave could play a greater role because all the reactants and intermediates are polar compounds, which are very good



<sup>\*</sup> Corresponding author. Tel.: +91 80 26615865; fax: +91 80 26426796. *E-mail address*: BHATYS@yahoo.com (Y.S. Bhat).

<sup>0021-9517/\$ -</sup> see front matter @ 2012 Elsevier Inc. All rights reserved. http://dx.doi.org/10.1016/j.jcat.2012.03.005

absorbers of microwave radiation. The main objective of the present study is to investigate the acylation of p-cresol with different aliphatic carboxylic acids mainly under microwave irradiation and to compare with conventional thermal heating. Further objective is to study the behavior of catalyst in the reactions carried out under microwave and conventional heating.

#### 2. Experimental

#### 2.1. Catalysts and chemicals

BEA zeolite in  $NH_4^+$  form (Si/Al = 30) was gifted by Süd-Chemie India Ltd. It was calcined in dry air for 8 h at 813 K to obtain protonic form of BEA zeolite. All other chemicals used in this study were procured from SD fine chemicals, India. *p*-Cresol and carboxylic acids were distilled before use, and all other chemicals were used without further purification.

#### 2.2. Characterization

Acidity of the fresh BEA sample and of those used in the reactions under conventional and microwave heating was measured by IR spectroscopy using pyridine as probe molecule. All the samples were activated by degassing at 383 K for 2 h and then saturated with pyridine. The catalyst samples were then evacuated at 423 K for 2 h to remove physisorbed pyridine. IR spectra of the samples were then recorded in the range 400–4000 cm<sup>-1</sup> using Bruker model Alpha-P IR spectrophotometer having resolution of 4 cm<sup>-1</sup> fitted with a diamond ATR cell. The catalyst samples used under microwave and conventional heating were also characterized by thermogravimetric analysis (TGA) to study the deactivation by coke precursors. TGA studies were carried out using a Mettler Toledo 851<sup>e</sup> star<sup>e</sup> 7.01 TGA/SDTA system. The temperature was ramped from 303 to 873 K at the rate of 5 K min<sup>-1</sup> under flowing air. Structural integrity of the catalyst samples after the reaction was checked by powder XRD. The data were recorded by stepscanning at  $2\theta = 0.025^{\circ}$  per step from  $3^{\circ}$  to  $40^{\circ}$  on Philips X'pert PRO X-ray diffractometer with graphite monochromatized Cu Ka radiation ( $\lambda = 1.5405$  Å).

#### 2.3. Catalytic reaction

Microwave-heated reactions were carried out in a microwave lab station 'START-S' having software that enables the on-line control of temperature of the reaction mixture with the aid of infrared sensor by regulation of microwave power output. All the reactions were carried out in a 50-mL closed glass vessel. All the reactions were stirred with the help of built-in automatic magnetic stirrer using Teflon stirring bar. Reactor vessel was kept in such a way that the reaction mixture was exactly in line with infrared sensor that monitors the temperature. Variable power up to 1000 W was applied by microprocessor-controlled single-magnetron system. The maximum irradiation power of 1000 W was utilized in the initial 1.0 min of the reaction to attain the temperature of 463 K, and then, lower power was used to maintain that temperature. Reactions under conventional heating were carried out in stainless steel autoclave fitted with 50-mL Teflon vessel. Autoclave was heated in a hot air oven with microprocessor-based temperature controller. In a typical reaction procedure, 20 mmol of p-cresol, 10 mmol of carboxylic acid, and 0.5 g of catalyst were taken in a reaction vessel. The reaction was carried out at desired temperature without using solvent. After the reaction, reaction mixture was dissolved in 15 g of toluene, stirred for about 30 min to extract adsorbed reactants and products, and filtered to separate the catalyst. Analysis of the reaction ingredients before and after the reaction was performed by Chemito GC1000 gas chromatograph using BP-20 capillary column (30 m  $\times$  0.32 mm) and flame ionization detector. The products were also analyzed and confirmed by GC-MS.

#### 3. Results and discussion

In order to find the optimum reaction conditions, effect of various parameters like reaction temperature, catalyst amount, reactant mole ratio, and reaction time was studied for acylation of *p*-cresol (PC) with hexanoic acid (HA) over BEA zeolite under microwave heating. Under optimum conditions, acylation of *p*-cresol with different carboxylic acids was studied under microwave as well as conventional heating over BEA zeolite.

#### 3.1. Acylation of p-cresol with hexanoic acid under microwave heating

#### 3.1.1. Effect of catalyst amount

Results of the effect of catalyst amount on the acylation of PC with HA are shown in Fig. 1. Under the conditions mentioned, PC did not react with HA in the absence of catalyst. Initially, conversion of HA increased with the catalyst amount, reached maximum with 0.5 g, and thereafter, it decreased slightly. Product distribution also varied with the amount of the catalyst. With lower catalyst amount, O-acylation was predominant, resulting in the formation of ester with only small amounts of C-acylated product (ketone). The amount of ester increased with the increase in catalyst amount, reached a maximum, and then decreased with concomitant increase in ketone concentration. Increase in catalyst amount are apparently due to increased number of catalytically active sites for the O-acylation of PC and subsequent Fries rearrangement of ester to ketone.

#### 3.1.2. Effect of temperature

The influence of temperature on the acylation of PC with HA was studied under otherwise similar conditions by varying temperature from 403 to 463 K, and the results are shown in Fig. 2. Temperature showed a marked effect on the conversion of HA and distribution of products. Conversion of HA increased with increase in temperature indicating endothermic nature of the reaction. At lower temperature, HA was more selective toward ester, but with increase in temperature, selectivity toward ketone increased. This suggests that O-acylation is favoured at lower temperature, and C-acylation, probably occurring through Fries rearrangement of the ester formed, is favoured at higher temperatures.



**Fig. 1.** Effect of catalyst amount on the acylation of p-cresol with hexanoic acid. Reaction condition: mole ratio PC: HA, 2:1; reaction time, 60 min; temperature, 463 K; max MW power, 1000 W.



**Fig. 2.** Effect of temperature on the acylation of p-cresol with hexanoic acid. Reaction condition: catalyst amount, 0.5 g; mole ratio PC:HA, 2:1; reaction time, 60 min; max MW power, 1000 W.

#### 3.1.3. Effect of mole ratio of reactants

Effect of mole ratio of reactants on conversion and selectivity was studied by varying the mole ratio of PC: HA from 3:1 to 1:3, other conditions being similar. Results are tabulated in Table 1. When the mole ratio of PC: HA was 1:1, 52% conversion of HA was observed with 58% and 42% selectivity toward ester and ketone, respectively. But the conversion of HA increased drastically to 77% with increased selectivity toward ketone (57%) when the amount of PC in the reaction mixture was doubled. Generally, acylation reaction occurs through formation of an acylium intermediate by protonation of nucleophilic carbonyl oxygen of carboxylic acid by Bronsted acid site of catalyst and subsequent attack of substrate by acylium ion [26]. Increased conversion of HA with increase in the amount of PC may be attributed to ready availability of PC for electrophilic attack by acylium ion. On the other hand, when the amount of HA was doubled, conversion of PC decreased to 45% with decreased selectivity toward ketone, which indicates the inhibitive effect of carboxylic acid on the reaction.

#### 3.1.4. Effect of reaction time

Conversion of HA as a function of reaction time under otherwise similar conditions is shown in Fig. 3. Conversion of HA was rapid in the beginning; 37% conversion with 100% selectivity toward ester was observed in first 3 min of the reaction. However, as the reaction proceeds, conversion increased slowly to a maximum of 80% at 180 min with decreased selectivity toward ester (37%), accompanied by an increase in ketone selectivity (63%). The initial selectivity toward ketone was zero, suggesting that it was not a primary product. The decrease in the concentration of ester with concomitant increase of the ketone suggests that it was not formed through direct acylation of aromatic ring, but through the Fries rearrangement of the primary product ester. BEA zeolite has been reported as a good catalyst for this type of rearrangement [17]. Conversion of ester to o-hydroxyketone seems to be favoured by ortho-directing effect of



**Fig. 3.** Effect of reaction time on the acylation of p-cresol with hexanoic acid. Reaction condition: catalyst amount, 0.5 g; mole ratio PC: HA, 2:1; temperature, 463 K; max MW power, 1000 W.

the hydroxyl group and stabilization of transition state and the product ketone by intramolecular hydrogen bonding between the hydrogen of hydroxyl and oxygen of the carbonyl group [27]. Possible mechanism of the reaction consistent with the above made observations is given in Scheme 1.

## 3.2. Acylation of p-cresol with different carboxylic acids under microwave and conventional heating

Effect of reaction time on the conversion of different carboxylic acids in the acylation of PC with acetic, propionic, butyric, hexanoic, octanoic, and decanoic acid was studied under optimum reaction conditions of temperature 463 K, mole ratio of PC: carboxylic acid 2:1 and catalyst amount of 0.5 g. Reaction time was varied from 3 to 240 min under microwave heating and 1–30 h under conventional heating. Conversion of different carboxylic acids as a function of reaction time under microwave and conventional heating is shown in Figs. 4 and 5, respectively.

Large difference in conversion was observed between two modes of heating. Under conventional heating, reaction proceeded very slowly, and at the end of 30 h, all the acids showed conversion of 10–20%. On the other hand, under microwave heating, conversion of different acids was in the range of 50–80%. The ester formed through O-acylation and ortho-hydroxyketone formed through Fries rearrangement of the ester were the only products. With all the acids, ester was initially formed followed by conversion to ortho-hydroxyketone. Selectivity of different acids toward ester and ortho-hydroxyketone after 240 min of reaction time is shown in Fig. 6.

The ketone/ester ratio increased with reaction time, and the equilibrium ratio in all the cases was higher than 1. Conversion of carboxylic acid increased with chain length up to hexanoic acid,

Table 1
Effect of mole ratio of reactants on the acylation of p-cresol with hexanoic acid

Mole ratio (PC: HA)	Conversion of HA (%)	Conversion of PC (%)	Yield of ester (%)	Yield of ketone (%)
3:1	78	_	34	44
2:1	77	-	33	44
1:1	52	-	30	22
1:2	-	45	32	13
1:3	-	42	30	12

Reaction condition: Catalyst amount, 0.5 g; reaction time, 60 min; temperature, 463 K; max MW power, 1000 W.



Scheme 1. Possible reaction mechanism for the acylation of p-cresol with carboxylic acid.



**Fig. 4.** Conversion of different carboxylic acids versus reaction time in the acylation of p-cresol under microwave heating. Reaction condition: catalyst amount, 0.5 g; mole ratio PC: carboxylic acid, 2:1; temperature, 463 K; max MW power, 1000 W.



**Fig. 5.** Conversion of different carboxylic acids versus reaction time in the acylation of p-cresol under conventional heating. Reaction condition: Catalyst amount, 0.5 g; mole ratio PC: carboxylic acid, 2:1; temperature, 463 K.

but decreased in the case of octanoic and decanoic acids. Variation of conversion with the chain length of the carboxylic acid could be attributed mainly to two factors that operate simultaneously, but in opposite directions. First factor is the stability of intermediate acyl cation, which increases with chain length of acid due to electron-donating effect of carbon chain, and the second factor is diffusion constraint, which increases with chain length of acid and limits the conversion [28,29]. It appears that up to hexanoic acid, the positive inductive effect of carbon chain predominates, and in case of octanoic and decanoic acids, diffusion limitations become a major factor.

#### 3.3. Catalyst deactivation and reusability

Reactions under microwave heating were not only faster but also showed higher conversion and selectivity when compared to conventional heating. Under conventional heating, conversion was very low initially, and with increase in reaction time, it increased gradually before reaching a value that is very much lower than the thermodynamic equilibrium value. This is an indication of catalyst deactivation. Color of the catalyst used under conventional



**Fig. 6.** Selectivity of different carboxylic acids toward acylated products under microwave heating. Reaction condition: catalyst amount, 0.5 g; Mole ratio PC: carboxylic acid, 2:1; temperature, 463 K; reaction time, 240 min.



Fig. 7. TGA plots of fresh and used BEA samples.

heating changed to dark brown, but the catalyst used under microwave changed to pale yellow at the end of the reaction. For further investigations, catalyst samples from the reaction of PC with HA under microwave and conventional heating were recovered after 4 and 30 h of the reaction and were, respectively, designated as BEAR(MW) and BEAR(CH). To recover the catalyst, reaction mixture was stirred with 15 g of toluene for 30 min; the solid phase was separated from the reaction mixture by filtration and dried at 393 K for 4 h before further use. Mass of catalyst recovered from the conventionally heated reaction, BEAR(CH), was found to be higher than the mass of catalyst sample used in the reaction, indicating coke/coke precursors built up on the surface. However, negligible change was observed in the mass of catalyst recovered from microwave-heated reaction, BEAR(MW). The recovered catalyst samples were characterized by TGA, IR, and XRD. Thermogravimetric analysis (TGA) plots of BEA, BEAR(MW), and BEAR(CH) samples are shown in Fig. 7. Initial weight loss of the samples up to 423 K is mainly due to removal of adsorbed moisture, whereas the weight loss above this temperature could be attributed to coke precursors [30]. It can be seen that at 873 K, percent weight loss of BEAR(MW) sample was just 2% higher than that of BEA sample, while that of BEAR(CH) sample was more than 20%. This clearly shows the presence of coke precursors on BEAR(CH) sample. Reusability of these samples was checked in the reaction of PC with HA under microwave as well as conventional heating, and the results are shown in Table 2. BEAR(MW) catalyst when reused under microwave heating showed similar conversion as that of fresh BEA zeolite, which shows that the catalyst was not deactivated in the microwave-heated reaction. But, BEAR(MW) catalyst when reused showed lower conversions similar to fresh BEA under conventional heating. BEAR(CH) when reused under conventional heating also showed very low HA conversion (5%), but under microwave

BEAR(CH) sample under microwave heating was found to be much
higher than that exhibited by fresh BEA zeolite under conventional
heating. This shows that the active sites of BEAR(CH) sample were
not completely deactivated by coke precursors. This was further
investigated by acidity measurements of the recovered catalyst
samples by IR spectroscopy in ATR mode using pyridine as probe
molecule. Chemisorbed pyridine on the Lewis and on the Bronsted
acid sites of zeolite BEA is revealed by characteristic bands at 1450
and 1545 cm <sup>-1</sup> , respectively. Intense peak at 1491 cm <sup>-1</sup> is ascribed
to the superposition of signals of Lewis and Bronsted adsorbed spe-
cies [31]. In the spectra displayed in Fig. 8, Bronsted acid peak of
BEAR(CH) sample was broadened with decreased intensity when
compared to BEA and BEAR(MW) samples, suggesting that the
Bronsted acid sites of this deactivated sample are decreased. Slight
shift in the 1545 cm <sup>-1</sup> peak suggests the presence of coke precur-
sors on the Bronsted sites. In order to check the regenerability,
BEAR(CH) sample was calcined at 813 K for 8 h and tested in the
reaction. Activity of this calcined sample was found to be similar
to fresh BEA zeolite. The structural integrity of the sample after cal-
cination was checked by X-ray diffraction. The XRD patterns of the
BEA, BEAR(CH), and BEAR(MW) catalysts as shown in Fig. 9 indi-
cate that the structure of the zeolite remains intact even after
the reaction.

heating showed 42% conversion of HA. Thus, the activity of

The foregoing studies show that the microwave heating is superior to conventional heating in all aspects of the reaction. Microwave irradiation not only accelerates the reaction rate but also enhances the activity and selectivity of BEA zeolite toward acylation and stabilizes the catalytic activity. On the other hand, under conventional heating, reactions were found to be sluggish from the beginning and finally resulted in very low yields due to catalyst deactivation. Similar lower conversions have been reported under conventional heating in the zeolite-catalyzed acylation of organic substrates with carboxylic acids [9]. These reactions are known to be inhibited initially by strong adsorption of reactants on the surface, followed by decomposition of resulting acylium ion to ketene, which can condense to diketene, and further polymerize to high-molecular-weight compounds ultimately blocking the active sites leading to deactivation of the catalyst [32].

Reaction of PC with carboxylic acid takes place in two steps first through direct O-acylation resulting in ester next by Fries rearrangement of ester to ortho-hydroxyketone. In order to understand the effect of microwave and conventional heating on these two reactions separately, direct Fries rearrangement of the ester, p-cresyl hexanoate, was investigated over BEA zeolite under microwave as well as conventional heating. The results obtained are shown in Figs. 10 and 11, respectively. Even though reaction proceeded at a faster rate under microwave heating, no difference in final conversion and selectivity was observed between the two modes of heating. Yield of ortho-hydroxy ketone obtained at the end of the reaction was found to be same as that obtained in direct reaction

Table 2					
Reusability	of fresh	and	used	BEA	catalysts.

Catalyst	Mode of heating	Conversion of HA (%)	Yield of ester (%)	Yield of ketone (%)
BEA	Microwave	80	28	52
BEAR(MW)	Microwave	77	28	49
BEAR(MW) calcined	Microwave	79	29	50
BEAR(CH)	Microwave	42	18	24
BEAR(CH) calcined	Microwave	78	29	49
BEA	Conventional	16	6	10
BEAR(MW)	Conventional	17	6	11
BEAR(CH)	Conventional	5	3	2

Reaction condition: Catalyst amount, 0.5 g; Mole ratio PC: HA, 2:1; temperature, 463 K. Microwave heating; reaction time, 240 min; max MW power, 1000 W. Conventional heating; reaction time, 30 h.



Fig. 8. IR spectra of pyridine adsorbed on (a) BEA, (b) BEAR(CH), and (c) BEAR(MW) samples.



Fig. 9. XRD patterns of (a) BEA, (b) BEAR(CH), and (c) BEAR(MW) samples.

of PC with HA under microwave heating. This clearly shows that the lower conversions observed under conventional heating in the reaction of PC with carboxylic acids are mainly due to inhibition of O-acylation reaction. Hence, the advantageous effects of microwave heating in the acylation of PC with HA must be due to its ability to prevent the initial inhibition of O-acylation that was observed under conventional heating.

#### 3.4. Promoting action of microwaves

In the reactions conducted under microwave irradiation, heating of reaction mixture depends on the ability of chemical materials used in the reaction to absorb microwave energy and subsequent release of this as heat energy. Heat-up time of different reactants and catalyst used in the reaction was measured in terms of time taken by a known quantity of compound to heat up to a particular temperature with constant microwave power of 1000 W. Time required to reach 373 K by different reactants, BEA zeolite, and water are given in Table 3. Heat-up time of different



**Fig. 10.** Fries rearrangement of p-cresyl hexanoate versus reaction time under microwave heating. Reaction condition: catalyst amount, 0.5 g; p-cresyl hexanoate, 10 mmol; temperature, 463 K; max MW power, 1000 W.

reactants was found to be in the order water < p-cresol < acetic acid < propanoic acid < butyric acid < hexanoic acid < octanoic acid < decanoic acid. Heat-up time of carboxylic acids increased with increase in chain length. However, the heating rate of reaction mixture containing p-cresol, carboxylic acid, and BEA zeolite was found to be same as that of p-cresol irrespective of the carboxylic acid. This mixture was heated to 373, 403, and 463 K in 17, 28, and 98 s, respectively, while the conventionally heated reaction required 35 min to reach 463 K. This difference in heating rate between two modes of heating was thought to be the reason for the lower conversion and formation of coke precursors in conventional heating. To check the effect of heating rate on conversion of HA, a set of reactions were conducted with different microwave programs, so that the desired temperature (463 K) was reached in different times, and the results are shown in Table 4. Same conversion was seen, and no deactivation of the catalyst samples was noticed irrespective of the heat-up time. This indicates that initial inhibition of O-acylation and subsequent formation of coke precursors under conventional heating are not due to slow heating of reaction mixture. But, microwave irradiation was found to have perceptible influence on the reaction rate. One important difference in the two methods of heating is generation of coke material on the catalyst



**Fig. 11.** Fries rearrangement of p-cresyl hexanoate versus reaction time under conventional heating. Reaction condition: catalyst amount, 0.5 g; p-cresyl hexanoate, 10 mmol; temperature, 463 K.

# Table 3 Time required to reach 373 K when 30 mmol of compound was heated at a constant MW power of 1000 W.

Compound	Time taken to reach 373 K (s)	Compound	Time taken to reach 373 K (s)
Acetic acid	20	Decanoic acid	116
Propanoic acid	25	p-Cresol	17
Butyric acid	31	Water	12
Hexanoic acid	49	BEA zeolite (4 g)	94
Octanoic acid	80	p-Cresol + Carboxylic acid + BEA zeolite	17

#### Table 4

Effect of heat-up time on the conversion of hexanoic acid.

Time to reach 463 K	Reaction time at 463 K (min)	Conversion of HA (%)
98 s	5	48
5 min	5	48
15 min	5	48
35 min	5	48

Reaction condition: Catalyst amount, 0.5 g; Mole ratio PC: HA, 2:1; temperature, 463 K. max MW power, 1000 W.

surface. The fact that no generation of coke material in the case of microwave heating leads one to say that the interaction of reactant molecules on the surface of the catalyst is certainly influenced by the method of heating.

In conventionally heated reaction, initial inhibition and coke formation are primarily observed in the O-acylation reaction, where both p-cresol and carboxylic acid are involved. It is reported that one of the main reasons for initial inhibition of the reaction is due to preferential adsorption of carboxylic acid [33]. p-Cresol is chiefly responsible for heating up of the reaction mixture as noticed by its low heat-up time. Consequently, the heat-up energy of p-cresol subsequently released to the medium might be affecting the adsorption of the carboxylic acid. This is probably responsible for the suppression of coke precursor formation on the surface of the catalyst. Due to this, the catalyst exhibits deactivation-free behavior. The role of the catalyst surface in this needs further investigation.

#### 4. Conclusions

Microwave heating was found to be superior to conventional heating in all aspects of the solventless acylation of p-cresol with different carboxylic acids over BEA zeolite. Microwave-heated reactions resulted in higher conversions of carboxylic acids with the formation of ester through O-acylation as the primary product followed by the Fries rearrangement to form ortho-hydroxy ketone. Present study showed that lower conversion observed under conventional heating was due to initial inhibition of O-acylation and catalyst deactivation. p-Cresol shows low heat-up times in the MW-heated reaction and is chiefly responsible for heating up of the reaction mixture. The preferential adsorption of carboxylic acid, which is known to be responsible for coke precursor formation, is probably affected by the heat-up energy released by p-cresol to the medium. This might have prevented the initial inhibition of Oacylation reaction as well as catalyst deactivation and allowed the catalyst to function with maximum activity and increased stability.

#### Acknowledgements

The authors thank the Principal and the Governing Council of Bangalore Institute of Technology for the facilities provided. Thanks are due to Süd chemie India Pvt Ltd. for providing zeolite sample. The authors would like to extend their thanks to Prof. PVK, BU for TGA and ATR facilities.

#### References

- M.G. Franck, J.W. Stadelhofer, in: Industrial Aromatic Chemistry, Springer, Berlin/Heidelberg, 1987.
- [2] H. van Koningsveld, J.J. Scheele, J.C. Jansen, Acta Crystallogr. C 43 (1987) 294.
   [3] A. Corma, Chem. Rev. 95 (1995) 559.
- [4] P. Marion, R. Jacquot, S. Ratton, M. Guisnet, in: M. Guisnet, J.P. Gilson (Eds.), Zeolites for Cleaner Technologies, Imperial College Press, London, 2002, p. 281.
- [5] J.B. Higgins, R.B. LaPierre, J.L. Schlenker, A.C. Rohrman, J.D. Wood, G.T. Kerr, W.J. Rohrbaugh, Zeolites 8 (1988) 446.
- [6] Jacobus C. Jansen, Edward J. Creyghton, Swie Lan Njo, Henk van Koningsveld, Herman van Bekkum, Catal. Today 38 (1997) 205.
- [7] Giovanni Sartori, Raimondo Maggi, Chem. Rev. 111 (2011) PR181.
- [8] P. Botella, A. Corma, J.M. Lopez-Nieto, S. Valencia, R. Jacquot, J. Catal. 195 (2000) 161.
- [9] J.M. Escola, M.E. Davis, Appl. Catal. A Gen. 214 (2001) 111.
- [10] Libor Cerveny, Katerina Mikulcova, Jiri Cejka, Appl. Catal. A Gen. 223 (2002) 65.
- [11] U. Freese, F. Heinrich, F. Roessner, Catal. Today 49 (1999) 237.
- [12] Dhanashri P. Sawant, S.B. Halligudi, Catal. Commun. 5 (2004) 659.
- [13] C. Guignard, V. Pedron, F. Richard, R. Jacquot, M. Spagnol, J.M. Coustard, G. Perot, Appl. Catal. A Gen. 234 (2002) 79.
- [14] P. Andy, J. Garcia-Martinez, G. Lee, H. Gonzalez, C.W. Jones, M.E. Davis, J. Catal. 192 (2000) 215.
- [15] Vasco F.D. Alvaro, Amadeu F. Brigas, Eric G. Derouane, Joao P. Lourenco, Bruna S. Santos, J. Mol. Catal. A: Chem. 305 (2009) 100.
- [16] C.L. Padro, C.R. Apesteguy, Catal. Today 107-108 (2005) 258.
- [17] A.J. Hoefnagel, H. van Bekkum, Appl. Catal. A Gen. 97 (1993) 87.
- [18] Mario G. Clerici, Top. Catal. 13 (2000) 373.
- [19] E. Heitling, F. Roessner, E. van Steen, J. Mol. Catal. A: Chem. 216 (2004) 65.
- [20] A.E.W. Beers, J.A. van Bokhoven, K.M. de Lathouder, F. Kapteijn, J.A. Moulijn, J. Catal. 218 (2003) 239.
- [21] C. Oliver Kappe, Angew. Chem. Int. Ed. 43 (2004) 6250.
- [22] J.P. Tierney, P. Lidström (Eds.), Microwave Assisted Organic Synthesis, Blackwell, Oxford, 2005.
- [23] A. Loupy (Ed.), Microwaves in Organic Synthesis, Wiley-VCH, Weinheim, 2006.
   [24] G. Bond, J.A. Gardner, R.W. McCabe, D.J. Shorrock, J. Mol. Catal. A: Chem. 278 (2007) 1.
- [25] Hiroshi Yamashita, Yumi Mitsukura, Hiroko Kobashi, J. Mol. Catal. A: Chem. 327 (2010) 80.
- [26] Matteo L.M. Bonati, Richard W. Joyner, Michael Stockenhuber, Micropor. Mesopor. Mater. 104 (2007) 217.
- [27] L.M. Jackman, M.M. Petrei, B.D. Smith, J. Am. Chem. Soc. 113 (1991) 3451.
- [28] B. Chiche, A. Finiels, C. Gauthier, P. Geneste, J. Org. Chem. 51 (1986) 2128.
- [29] S.G. Wagholikar, P.S. Niphadkar, S. Mayadevi, S. Sivasanker, Appl. Catal. A Gen. 317 (2007) 250.
- [30] Baodong Wang, George Manos, J. Catal. 250 (2007) 121.
- [31] J.P. Marques, I. Gener, P. Ayrault, J.C. Bordado, J.M. Lopes, F. Ramoa Ribeiro, M. Guisnet, Micropor. Mesopor. Mater. 60 (2003) 251.
- [32] D. Rohan, C. Canaff, P. Magnoux, M. Guisnet, J. Mol. Catal. A: Chem. 129 (1998) 69.
- [33] E.A. Gunnewegh, R.S. Downing, H. van Bekkum, L. Bonneviot, S. Kaliaguine, A refined tool for designing catalytic sites, Stud. Surf. Sci. Catal. 97 (1995) 447.