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Active and deactive modes of modified montmorillonite in *p*-cresol acylation



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ABSTRACT

para-Toluene sulphonic acid (p-TSA)-treated montmorillonite clay used as heterogeneous catalyst in acylation of para-cresol (PC) with aliphatic carboxylic acids. Reactions were studied under microwave and conventional modes of heating and reaction conditions were optimized by varying mole ratio, temperature, amount of catalyst and reaction time. Under optimized conditions the reaction was carried out involving p-cresol and decanoic acid. The reaction involved two steps, O-acylation involving ester formation followed by the Fries rearrangement involving C-acylation resulting in ketone product. Microwave heating mode showed higher conversion and the catalytic activity almost retained in repeated use. On the other hand the catalytic activity dropped by more than 50% in the case of conventional heating indicating rapid deactivation. A change in the color of the used catalyst was more intense in the case of conventional than in the microwave heating. Used catalysts were characterized for surface area and pore volume by BET technique, acidity by FTIR spectroscopy and amount of coke by TGA. Further investigations on the catalyst used in conventional heating revealed that the deactivation occurred during the O-acylation and not in the subsequent Fries rearrangement. However, the catalyst in the microwave irradiated reaction, exhibited a retarded rate of formation of coke precursors on the surface during O-acylation, thus preventing any decrease in catalytic activity. Present study indicates that the technique chosen for heating the reaction medium plays an important role in suppressing deactivation.

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1. Introduction

The acylation of phenolic compounds is an important route for the synthesis of aromatic ketones that are intermediates in the manufacturing of fine and specialty chemicals. Direct acylation of hydroxyl group yields ester, which converts to ketone by subsequent Fries rearrangement. Both ester and ketone formed in the reaction are valuable intermediates in the synthesis of pharmaceuticals and fragrances [1–4]. The reaction occurs by interaction of the phenolic compound with carboxylic acids in the presence of an acid catalyst and involves an intermediate acylium ion generated by protonation of acylating agent and subsequent dehydration [5]. In the present industrial practice, most of the acylation reactions are carried out using corrosive Lewis acid catalysts, such as AlCl₃, HF, BCl₃, FeCl₃, ZnCl₂, SnCl₄ and TiCl₄ which are required in stoichiometric amounts and generate substantial amount of waste products [1,6–8]. Efforts have been made to replace these acids by reusable, eco-compatible, heterogeneous solid acids like zeolites [1], acidic

http://dx.doi.org/10.1016/j.molcata.2014.05.017 1381-1169/© 2014 Elsevier B.V. All rights reserved. clays [9,10] and heteropoly acids [11,12]. It is also desirable to use less hazardous acylating agents like carboxylic acids instead of acyl halides and anhydrides.

Acidic zeolites, heteropoly acids, metal oxides and cation exchanged clays are the most studied heterogeneous catalysts for the direct acylation. Activity and selectivity of these catalysts have been investigated in the direct acylation of several organic substrates like toluene, biphenyl and naphthalene, aromatic ethers like anisole, thioanisole, veratrole, and 2-methoxy naphthalene, heterocyclic compounds like thiophene, benzofuran and phenolic compounds like phenol, PC, naphthol and resorcinol [7,10,12,13].

Among various solid acid catalysts employed in organic synthesis, acidic clays are exclusive because of their abundant availability and easy modification. Acidity in clays can be generated mainly by cation exchange and acid treatment. Exchange with several cations and *p*-TSA treated montmorillonite clay possess strong Lewis and Bronsted acidic sites compared to other solid acids [6,14]. One of the major problems in acylation using clays is lower conversion and longer duration in the liquid phase conventional heating process [11].

Emphasis of the present work is to study the effect of mode of heating on the mechanism of deactivation and on the chain length

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of the acylating agent for the formation of ester and ketone on a *p*-TSA treated montmorillonite clay catalyst. This particular catalyst was selected for its high acidity, large surface area and easy accessibility to the active site.

2. Experimental

2.1. Catalyst and chemicals

Surface and acidity modification of montmorillonite clay was carried out by treating with *p*-TSA using the procedure reported earlier [6,14].

It involved treatment of the montmorillonite obtained from Bhuj area, Gujarat, India. The clay was converted to sodium form by 1 M NaCl solution treatment. The composition was found using XRF to be 42.86% SiO₂, 16.64% Al₂O₃, 10.05% Fe₂O₃, 2.58% MgO, 1.92% Na₂O, 0.41% K₂O and 1.79% CaO with idealized structural formula Si₄[Al_{1.348}Fe_{0.386}Mg_{0.266}]O₁₀(OH)₂Na_(0.324) [6].

Chemicals used in this study were procured from SD fine chemicals, India. PC and carboxylic acids were distilled before use and all other chemicals were used without further purification.

2.2. Characterization

The *p*-TSA treated clay catalyst samples were characterized for acidity, surface area, X-ray diffraction (XRD) and thermogravimetric analysis (TGA) before and after the reactions.

Acidity was measured by FT-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. FT-IR spectra of the samples were then recorded in the range 1400–1600 cm⁻¹ using Bruker model Alpha-P IR spectrophotometer having resolution of 4 cm⁻¹ fitted with a diamond ATR cell [15,16].

Surface area measurements were carried out using Quanta chrome Nova-1000 surface analyzer under liquid nitrogen temperature [6,14].

The catalyst samples used in reactions under microwave and conventional heating were also characterized by TGA to study the deactivation by coke precursors. TGA studies were carried out using a Mettler Toledo 851e stare 7.01 TGA–DTA system. The temperature was ramped from 303 to 873 K at the rate of 5 K min⁻¹ under flowing air [17,18].

Structural integrity of the catalyst samples after the reaction was checked by powder XRD. The data were recorded by step scanning at $2\theta = 0.020^{\circ}$ per step from 3° to 80° on Shimadzu MAXima_X XRD-7000 X-ray diffractometer with graphite monochromatized Cu K α radiation (k = 1.5406 Å) [15,16].

2.3. Catalytic tests

Microwave heating. Ten millimoles of PC and 5 mmol of aliphatic carboxylic acid were mixed with 1 g catalyst in a microwave reactor vessel with magnetic stirring. Reactor vessel was kept in 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 in such a way that the reaction mixture was exactly in line with infrared sensor that monitors the temperature. Variable power up to 1200 W was applied by microprocessor-controlled single-magnetron system. The maximum irradiation power of 1200 W was used in the initial 1 min of the reaction to attain the temperature of 463 K, and then, variable power (500–700 W) from the reactor auto-maintains that temperature. The reaction mixture was then cooled for 10 min, followed by addition of 10 ml of toluene, stirred for about 30 min



Fig. 1. Effect of catalyst amount on the acylation of PC with DA. Reaction condition: mole ratio PC:DA, 2:1; reaction time, 60 min; temperature, 463 K.

to extract adsorbed reactants and products and filtered to separate the catalyst. Analysis of the ingredients before and after the reaction was carried out using Chemito GC-1000 gas chromatograph with TR-WAX capillary column (30 m length, thickness 0.32 mm and 0.5 μ m internal diameter) and flame ionization detector. The products were also analyzed and confirmed by GC-MS [1,14].

Conventional heating. Same amount of reactants and catalyst were taken as in microwave heating in a 50 ml vessel placed in a hot-air oven at 463 K for about 16 h. After the completion of the reaction, analysis was performed as given under the microwave heating.

3. Results and discussion

In order to optimize the reaction conditions, various parameters like effect of reaction temperature, catalyst amount, mole ratio of the reactants and reaction time for acylation of PC with DA over *p*-TSA clay were studied. Under optimum conditions, acylation of PC with different carboxylic acids was investigated under microwave as well as conventional heating over *p*-TSA clay as catalyst.

3.1. Acylation of PC with DA under microwave heating

3.1.1. Effect of catalyst amount

No reaction was observed between PC and carboxylic acids in the absence of catalyst. Under the specified conditions, increase in the conversion of DA was observed with the increase in the catalyst amount from 0.1 to 0.5 g and thereafter it decreased slightly. At low catalyst amounts, O-acylation (ester) dominated with small amount of C-acylated (ketone) product. Fig. 1 shows that the conversion of acid to ester improved with the increase in catalyst amount and reached a maximum at 0.5 g. When the ester concentration increases and reaches an optimum value, formation of ketone increases through the rearrangement of the ester. This reaction takes place at an enhanced rate with catalyst quantity higher than 0.5 g as more number of acid sites are available. There is a simultaneous hydrolysis of ester forming DA and *p*-cresol thus showing a lower conversion of DA.

3.1.2. Effect of temperature

Temperature has a significant effect on the catalytic acylation of PC with DA. Effect of temperature was studied under the same conditions by varying temperature from 403 to 463 K. The results are shown in Fig. 2. It was observed that at lower temperatures (433 K), DA conversion is more selective toward ester and the selectivity toward ketone increased as the temperature was raised beyond



Fig. 2. Effect of temperature on the acylation of PC with DA. Reaction condition: catalyst amount, 1 g; mole ratio PC:DA, 2:1; reaction time,60 min.

450 K. This suggests that ketone formation takes place through the Fries rearrangement of ester and is favored at higher temperature [1].

3.1.3. Effect of mole ratio

The molar ratio of PC to DA was changed from 3:1 to 1:3 with 1 g of clay catalyst at reaction temperature of 463 K. Table 1 summarizes results of these experiments. When the mole ratio of PC: DA was 1:1, 40% conversion of DA was observed with 75% and 25% selectivity toward ester and ketone, respectively. Further increase in PC shows an increase in conversion of DA. At 2:1 mole ratio of PC: DA, 52% of conversion of DA with 38% selectivity for ester and 62% selectivity for ketone were observed. Generally, acylation reaction occurs through protonation of carbonyl oxygen of carboxylic group by the Bronsted acid sites forming an acylium ion which gets attacked by the readily available PC in the reaction mixture [17]. On the other hand, conversion of PC decreased to 36% when the amount of DA was doubled. This indicates the inhibitive effect of carboxylic acid on the reaction [1].

3.1.4. Effect of reaction time

Reaction time as a function of conversion of DA under similar reaction conditions are shown in Fig. 3. Initially, conversion of DA was observed to be 52% with 85% selectivity toward ester. As the reaction proceeds, the conversion of DA gradually increased and attained thermodynamic equilibrium at 240 min with a maximum of 62% in. The selectivity toward ketone was as low as 15% in the first 10 min and as the reaction proceeds, selectivity toward ketone increased to 63% with a simultaneous decrease in selectivity toward ester (37%). This suggests that ester was the primary product and enhancement in the concentration of ketone with concomitant decrease of ester indicated that ketone is not obtained

Table 1	
Effect of mole ratio on the acylation of PC with DA.	

PC:DA (mmol)	Conversion of DA (%)	Conversion of PC (%)	Reactant conversion toward	
			Ester (%)	Ketone (%)
15:5	53	-	23	30
10:5	52	-	20	32
5:5	40	-	30	10
5:10	-	36	25	11
5:15	-	32	23	9

Reaction condition: catalyst amount 1g; reaction time 60 min and temperature 463 K under MW irradiation.



Fig. 3. Effect of reaction time on the acylation of PC with DA. Reaction condition: catalyst amount, 1 g; mole ratio PC:DA, 2:1; temperature, 463 K.

by the direct acylation of aromatic ring, but forms through Fries rearrangement of primary ester product.

Earlier studies have reported that acid treated clays are good catalysts for the Fries rearrangement [12,19]. Conversion of ester to *ortho*-hydroxyketone was favored owing to the presence of strong ortho directing hydroxyl group and to the formation of intra-molecular hydrogen bonding between carbonyl oxygen and hydrogen of hydroxyl group [20]. Possible reaction mechanism is given in Scheme 1.

3.2. Acylation of PC with various carboxylic acids under MW and conventional heating

Under optimized conditions, the effect of different modes of heating on reaction time was studied for acylation of PC with acetic, propionic, butyric, hexanoic, octanoic and decanoic acids at 463 K with 1 g of catalyst and carboxylic acid:PC mole ratio of 1:2. Reaction time was varied from 5 to 240 min and 1 to 40 h under microwave and conventional heating respectively. Conversion of different carboxylic acids as a function of reaction time under microwave and conventional heating are shown in Fig. 4(a) and (b) respectively. The increase in conversion from acetic acid to decanoic acid is due to the enhanced inductive effect with increase in carbon chain length.

Difference in conversion was observed between two modes of heating. Under conventional heating, reaction proceeded very slowly and at the end of 10 h, all the acids showed conversion between 12 and 20%. On the other hand, under microwave heating, conversion of different acids was in the range of 40–58% in 60 min.

Microwave heating showed more conversion toward ester of all the acids in the beginning. Further increase in the parameters like temperature, catalyst amount, reaction time and mole ratio alters the ratio of ester to ketone; a maximum of 42% ketone was observed under microwave heating. In the case of conventional heating, the conversion of acid showed a maximum of 35%, in which 30% got converted to ester and the rest of it to ketone. Beyond this point any increase in temperature, time and the catalyst amount had no effect on the ratio of ester to ketone.

3.3. Catalyst deactivation

Higher catalytic activity and selectivity were observed in the microwave heating with shorter reaction times compared to the conventional heating mode. Maximum yield of the products observed in the case of MW irradiation was not achieved in case



Scheme 1. Possible reaction mechanism with catalyst for the acylation of carboxylic acid with PC.

of conventional heating after 40 h. The color of recovered catalysts after the reaction under conventional and microwave heating were observed to be dark brown and pale green respectively, possibly due to formation of coke precursors. Further investigation was carried out on the recovered catalyst samples from the reaction between PC and DA for 180 min in the case of MW irradiation and for 40 h in the case of conventional heating. These were respectively designated as *p*-TSAC(MW) and *p*-TSAC(CH). The catalyst recovery was done by separating the used catalyst from the reaction mixture



Fig. 4. Conversion of different carboxylic acids versus reaction time in the acylation of PC under (a) microwave heating and (b) conventional. Reaction condition: catalyst amount, 1 g; mole ratio PC: carboxylic acid, 2:1; temperature, 463 K.

followed by washing with 15 g of toluene, filtered and then dried in hot air oven for 3 h at 393 K.

The recovered catalysts were again used in the reaction between PC and DA under optimized conditions in the conventional as well as microwave heating. The results are presented in Table 2.

The catalyst *p*-TSAC(MW) when used under both microwave and conventional heating showed almost same activity as fresh *p*-TSAC, but *p*-TSAC(CH) catalyst when used under conventional heating shows less than 8% conversion. On the other hand, *p*-TSAC(CH) when used in MW heated reaction, showed similar activity as *p*-TSAC(MW) used in conventional heating mode. The results clearly demonstrate that microwave mode of heating suppressed the deactivation maintaining the same activity as the fresh catalyst. However, conventional heating accelerated the deactivation process resulting in lower catalytic activity.

Further the recovered catalysts *p*-TSAC(CH) and *p*-TSAC(MW) were characterized using TGA–DTA, pyridine FT-IR, XRD and for BET surface area to investigate the changes brought about in the catalytic characteristics after the reaction by the two modes of heating.

BET surface area was measured for both the catalyst samples before and after the reaction in the two modes of heating. Both samples, fresh and the used one in microwave heating showed almost the same specific surface area of about 130 m². On the other hand, there was a substantial decrease (to the extent of 30%) in the surface area of the used catalyst sample in the conventional mode of heating compared with the fresh one and also the one used in MW heated reaction. The decrease in surface area of catalyst sample *p*-TSAC(CH) showed that deactivation of catalyst did occur mainly in conventional mode of heating. Negligible change in the surface area

Table 2

Comparison of conversion of DA with the fresh and used catalyst samples recovered after the reaction.

Catalyst	Mode of heating	Conversion of DA (%)	Reactant conversion toward	
			Ester (%)	Ketone (%)
p-TSAC (fresh)	Microwave	57	22	35
p-TSAC (MW)	Microwave	53	21	32
p-TSAC (CH)	Microwave	21	16	5
p-TSAC(fresh)	Conventional	26	19	7
p-TSAC (MW)	Conventional	24	18	6
p-TSAC (CH)	Conventional	8	6	2

Reaction condition: catalyst amount, 1 g; mole ratio PC:DA, 2:1; temperature, 463 K. Microwave heating; reaction time, 120 min; conventional heating; reaction time, 40 h.



Fig. 5. TGA-DTA plots of p-TSAC fresh, p-TSAC(MW) and p-TSAC(CH).

between the fresh *p*-TSAC and *p*-TSAC (MW) catalyst samples leads to the conclusion that the surface is not significantly covered by the species responsible for the deactivation.

The TGA plots of fresh *p*-TSAC, *p*-TSAC(MW) and *p*-TSAC(CH) are shown in Fig. 5. Initial weight loss up to 150 °C was attributed to the loss of water molecules coordinated to interlayer cations [6]. *p*-TSAC(MW), in general, showed almost similar weight loss as that of fresh *p*-TSAC indicating negligible presence of the species responsible for the color change. On the other hand, *p*-TSAC(CH) showed a considerable weight loss (about 15%) than fresh *p*-TSAC evidently due to presence of coke precursor in the former catalyst.

XRD pattern of fresh *p*-TSAC, *p*-TSAC(MW) and *p*-TSAC(CH) is shown in Fig. 6. The patterns clearly show no significant change in structural integrity of the catalyst samples before and after the reaction conducted in different heating modes.

Pyridine-FT-IR spectra of *p*-TSAC, *p*-TSAC(MW) and *p*-TSAC(CH) are shown in Fig. 7. The fresh *p*-TSAC showed three different peaks at 1550, 1445 and 1490 cm⁻¹ due to Bronsted, Lewis and both Lewis and Bronsted type respectively. Acylation reaction is a Bronsted acid catalyzed reaction. There is negligible change in the Bronsted acidity before and after the reaction under microwave heating. Whereas the catalyst used under conventional heating showed significant changes in the FT-IR pattern. The peak corresponding to Bronsted acidity almost disappeared and the one corresponding to Lewis acidity in the catalyst used under microwave heating. This could be due to some adsorbed carbonaceous species in very low concentration as evident by the change in color of the catalyst from off white to pale green. While in conventional heating color of the catalyst becomes dark brown due to the presence of coke



Fig. 6. XRD pattern of (a) p-TSAC fresh, (b) p-TSAC(MW) and (c) p-TSAC(CH).



Fig. 7. Pyridine FT-IR spectra of *p*-TSAC fresh, *p*-TSAC(MW) and *p*-TSAC(CH).

precursors in high concentration. The loss of Bronsted acidity in the case of *p*-TSAC(CH) was clearly responsible for its low activity in the acylation reaction. On the other hand, small changes in the Bronsted acidity in *p*-TSAC(MW) explains its retention of high activity. In both the used catalysts, additional peak around $1510 \,\mathrm{cm^{-1}}$ was attributed to the adsorbed species on the catalyst.

3.4. Role of catalyst in Fries rearrangement

Reaction of PC with carboxylic acid takes place in two steps first through direct O-acylation resulting in ester, followed by Fries rearrangement of ester to ortho-hydroxyketone. In order to understand the effect of microwave and conventional heating on the catalyst deactivation in both the steps, direct Fries rearrangement of the ester, p-cresyldecanoate, was investigated with fresh p-TSAC under both the modes of heating. The results obtained are shown in Fig. 8(a) and (b) respectively. The trend of the reaction shows conversion of the ester into PC, DA and ketone in both cases [21]. However, in the case of microwave mode of heating, the conversion of the ester to ketone is found to be higher at any given point of time Fig. 8(a). This indicates that the Fries rearrangement is more facile in presence of microwave than in the conventional mode of heating. For example, at 180 min under microwave heating, the ester showed a total conversion of 69% out of which 31% was found to be toward ketone and 38% toward DA and PC whereas, in conventional heating 15% of ketone with 50% of DA and PC were found to be formed in 40 h. Further, in both cases, the conversion of the reactant ester was high and observed to be almost same (about 65%) which shows that there is no catalyst deactivation in both the modes of heating. This leads to the conclusion that the deactivation of the catalyst in acylation reaction under conventional mode of heating is mainly due to the ester formation reaction and not due to the Fries rearrangement.

Chandrashekara et al. [1] have reported that the coke formation in acylation reactions is primarily due to the intermediate acylium ions formed during the esterification step. In the present reaction studied with *p*-TSAC, acylium ions are expected to be formed during the esterification step which apparently causes the catalyst deactivation.

3.5. Retardation of catalyst deactivation in microwave irradiation

In acylation reaction, acylium ion is generated by the protonation and dehydration of carboxylic acid. This acylium ion oriented on the polar acid sites of catalyst in a specific way leads to



Fig. 8. Fries rearrangement of *p*-cresyl decanoate versus reaction time under (a) MW heating, and (b) conventional heating. Reaction conditions: catalyst amount, 0.5 g; *p*-cresyldecanoate, 10 mmol; temperature, 463 K.

formation of ketene and polymerization of ketene leads to higher hydrocarbon, which covers the active sites and deactivates the catalyst [1,23]. Although acylium ions are formed in microwave heating, their effect in causing deactivation probably is reduced in presence of microwaves. The microwave radiations apparently favor the non-promotion of coke precursors being formed from the acylium ions favoring the esterification and further conversion of ester to ketone. Influence of microwave heating mode in suppression of coke precursor formation was confirmed by measuring the time required to reach the reaction temperature by individual reactants and reaction mixture. Measured values are given in Table 3. The values showed that the time required to reach

Table 3

Time required reaching 373 K, when 30 mmol of individual compound was heated at a constant power of 1200 W under microwave heating.

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	p-TSA clay (4g)	94
Octanoic acid	80	<i>p</i> -Cresol + decanoic acid + <i>p</i> -TSA clay	57

Table 4

Effect of heating rate on the conversion of decanoic acid.

Time to reach 463 K	Reaction time at 463 K (min)	Conversion of DA (%)
123 s	10	50
5 min	10	50
10 min	10	50
30 min	10	50
60 min	10	50

Reaction condition: catalyst amount, 1 g; mole ratio PC:DA, 2:1; temperature, 463 K.

a preset temperature followed the order, decanoic acid > octanoic acid > hexanoic acid > butyric acid > propanoic acid > acetic acid > *p*cresol > water. However time required for the reaction mixture consisting *p*-cresol, carboxylic acid [1] and *p*-TSA clay was almost same irrespective of the carboxylic acids. It is important to note that *p*-cresol with decanoic acid along with the catalyst required 58 s and 40 min in microwave and conventional heating mode respectively. Heating time to reach reaction temperature of 463 K was varied from 123 s to 60 min in microwave mode. After reaching 463 K the reaction mixture was maintained at this temperature for 10 min in all the cases. Results are given in Table 4. It is quite evident from this table that irrespective of heating time required to achieve the pre-set reaction temperature, conversion of the reactant decanoic acid remained the same (50%) indicating suppression of coke precursors from acylium ion.

According to Kappe et al. [22], in the majority of cases the reason for the observed rate enhancements is a purely thermal/kinetic effect, that is, a consequence of the high reaction temperatures that can rapidly be attained when irradiating polar materials in a microwave field. Present study, however, reveals yet another aspect of the effect of microwaves on the reaction path wherein the formation of coke precursors, in some way, is retarded by the microwaves. The acylium ions adsorbed on the polar acid sites of the clay have less time to orient themselves to generate coke precursors but enough time for the interaction with PC to form the ester. Apparently, microwaves cause the polar acid sites to change their orientations with the magnetic field not allowing the acylium ions to position themselves to facilitate the formation of coke precursors.

4. Conclusions

Higher catalytic activity was observed in the microwave irradiated reaction with a significantly short reaction time compared with conventional heating mode in all aspects of the solvent-less acylation of PC with DA over *p*-TSAC. The reaction mechanism was similar between the two modes of heating but exhibiting an increased rate of reaction in microwave heating mode. Lower conversion observed under conventional heating was attributed to catalyst deactivation caused by the acylium ions accelerating formation of coke precursors.

Several reports on microwave induced reactions suggest that the enhancement in the rate is a consequence of rapid attainment of high temperatures in the reaction medium comprising polar materials and is purely a thermal/kinetic effect. Present study on acylation reveals yet another aspect of the effect of microwaves on the reaction path wherein the formation of coke precursors, in some way, is retarded by the microwaves. The acylium ions adsorbed on the polar acid sites of the clay probably have less time to orient themselves for the formation of coke precursors but enough time for the interaction with PC to form the ester. Apparently, microwaves cause the polar acid sites to change their orientations with the magnetic field not allowing the acylium ions to position themselves to facilitate the formation of coke precursors.

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