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Atom efficient Friedel–Crafts acylation of toluene with propionic anhydride over solid mesoporous superacid UDCaT-5

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A R T I C L E I N F O

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Friedel–Crafts acylation is ubiquitous in industry and is typically carried out by using more than stoichiometric quantities of homogeneous catalysts. This creates pollution. In this work, acylation of toluene was studied in liquid phase with propionic anhydride with a variety of solid superacids to produce 4′-methylpropiophenone (4′-MPP). The solid superacids were modified versions of zirconia, namely, UDCaT-4, UDCaT-5 and UDCaT-6 developed in our laboratory; amongst which UDCaT-5 was the most active, selective and robust catalyst. The effects of various reaction parameters on the rate of reaction and selectivity were investigated to deduce the intrinsic kinetics of the reaction. The reaction is free from any external mass transfer as well as intraparticle diffusion limitations and is intrinsically kinetically controlled. The acylation conditions were: temperature 180 °C, toluene to propionic anhydride molar ratio 5:1, catalyst loading 0.06 g cm^{-3}, speed of agitation 1000 rpm, under autogenous pressure in a stainless steel autoclave reactor. Propionic acid generated *in situ* also reacts sequentially with toluene to give 4′-MPP. A conversion of 62% of priopionic anyhydride is obtained after 3 h, with 100% mono-acylated product containing 67% 4′-MPP. Water is the only co-product of the overall reaction. A suitable kinetic model was developed. The reactions were carried out without using any solvent in order to make the process cleaner and greener.

1. Introduction

Liquid acids have been extensively used as catalysts in a variety of chemical and allied industries. Green chemistry approach involves the replacement of corrosive and toxic liquid acids such as HF and H_2SO_4 by environmentally benign heterogeneous solid acids. The production of various pharmaceuticals, agrochemicals, dyes and pesticides involves the synthesis of aromatic ketones and their derivatives. The common routes for preparation of these ketones proceed *via* Friedel–Crafts acylation of the concerned aromatic hydrocarbon with derivates of carboxylic acids, which are traditionally catalyzed by either Lewis acids such as $AlCl_3$, $FeCl_3$ and BF_3 or Brønsted acids such as HF or H_3PO_4 [1]. 4′-Methylpropiophenone (4′-MPP) is found to have wide applications in the area of fine chemicals, pharmaceuticals, resins, drugs, perfumes and specialty chemical synthesis. The classical production of 4′-MPP is performed by Friedel–Crafts acylation process of toluene with propionic anhydride or propionyl chloride, using stoichiometric quantities of conventional homogeneous Lewis acid catalyst, $AlCl_3$, $FeCl_3$ or BF_3 [2]. Use of these catalysts is fraught with a numerous drawbacks and operational problems. More than stoichiometric amount of Lewis acid is required. The reaction complexes formed are rather stable and their break-up to obtain the desired product leads to the loss of the catalyst [1,3]. The corrosive nature of homogeneous acids results in premature ageing of the processing equipment and associated transfer lines, which is expensive. Use of solid acids such as shape selective zeolites in acylation with carboxylic acids is more attractive [4].

In recent years, efforts have been directed toward the promotion of solid acid catalysts and several synthetic procedures have been reported. Heterogeneous solid acids are advantageous over conventional homogeneous acid catalysts [5–7]. They are non-corrosive; presenting fewer disposal problems, and their separation from fluid phase is much easier, which allows their repeated use. They permit the use of cheaper and non-polluting reagents, and offer several different reactor configurations [3]. In addition, physical and chemical properties of solid acids can be tailored and tuned to promote reactivity and selectivity and prolonged catalyst life [7]. Nakamura et al. [8] described the propionylation and butyrylation of toluene with propionic anhydrides and butyric anhydrides over SO_4/ZrO_2, SO_4/SnO_2, Pt-SO_4/ZrO_2, and Ru-SO_4/ZrO_2; yields of 7–9% *o*- and 91–93% *p*-isomers were 31, 26, 32, and 44% for propionylation and 46, 29, 44, and 55% for butyrylation, respectively obtained.

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Nomenclature

A	limiting reactant species A, propionic anhydride
B	excess reactant species B, toluene
C_i	concentration of species 'i' (mol cm^{-3})
E	apparent activation energy (kcal mol^{-1})
k	rate constant (cm^6 gcat^{-1} mol^{-1} s^{-1})
k_0	frequency factor (cm^6 gcat^{-1} mol^{-1} s^{-1})
k_1	rate constant of reaction (1) (cm^6 gcat^{-1} mol^{-1} s^{-1})
k_2	rate constant of reaction (2) (cm^6 gcat^{-1} mol^{-1} s^{-1})
k_3	rate constant of reaction (3) (cm^6 gcat^{-1} mol^{-1} s^{-1})
k_4	rate constant of reaction (4) (cm^6 gcat^{-1} mol^{-1} s^{-1})
k_5	rate constant of reaction (5) (cm^6 gcat^{-1} mol^{-1} s^{-1})
k_6	rate constant of reaction (6) (cm^6 gcat^{-1} mol^{-1} s^{-1})
P_1	propionic acid
P_2	2′-methylpropiophenone (2′-MPP)
P_3	3′-methylpropiophenone (3′-MPP)
P_4	4′-methylpropiophenone (4′-MPP)
$-r_i$	rate of reaction of species 'i' (mol gcat^{-1} s^{-1})
S_{P_4}	selectivity of desired product, 4′-methylpropiophenone (4′-MPP)
T	temperature (K)
t	time (s)
W	water
w	catalyst loading (g cm^{-3} of liquid phase)

Subscripts

1	reaction (1)
2	reaction (2)
3	reaction (3)
4	reaction (4)
5	reaction (5)
6	reaction (6)
i	species
P_4	4′-methylpropiophenone (4′-MPP)

Our laboratory has been pursuing the development of new ecofriendly solid acid catalysts for several industrially relevant reactions including process kinetics and reactor design. The activities and selectivities of different solid acid catalysts have been successfully evaluated in our laboratory for developing green Friedel–Crafts acylation and alkylation reactions. Alkylation of a variety of aromatic compounds was studied over solid superacids using different alkanols [9–12]. Among them, solid superacidic UDCaT series catalysts have received the most attention due to their unique structure and strong acidity. Flexibility in their acid strength, low toxicity and fairly high thermal stability make them excellent and versatile catalysts for a wide variety of acid catalyzed reactions in homogeneous and heterogeneous media [13–17]. We prepared mesoporous superacids named as UDCaT-4, UDCaT-5 and UDCaT-6, which are modified versions of zirconia and have found a great potential for industrially important reactions [14–16]. We have reported, for the first time, that a sulfated zirconia, with sulfur content as high as 9% (w/w), was produced with preservation of tetragonal phase by using chlorosulfonic acid as a new source for sulfate ion. It was designated as UDCaT-5 [15]. The name of the catalyst "UDCaT" symbolizes the authors' research institute, University Department of Chemical Technology (UDCT), which is now renamed as Institute of Chemical Technology (ICT). The work summarizes the investigation of activity of these new breed of catalytic materials in atom efficient Friedel–Crafts acylation of toluene with propionic anhydride under solventless conditions, including reaction kinetics.

The objective of the present work was to evaluate the solid superacid of UDCaT series of catalysts and to achieve the production of 4′-MPP by direct propionylation of toluene with propionic anhydride. A systematic investigation of the effects of various operating parameters is presented. A mathematical model is developed to describe the reaction pathway and validated with experimental results. The overall process is green and clean.

2. Experimental

2.1. Chemicals

Toluene, propionic anhydride, zirconium oxychloride, aluminum nitrate, ammonium persulfate and aqueous ammonia solution were procured from Aldrich, USA. Hexadecyl amine and chlorosulfonic acid was purchased from Spectrochem Ltd. Mumbai, India. Tetraethyl orthosilicate (TEOS) was procured from Fluka, Germany. All chemicals were of analytical reagent (A.R.) grade. These were used as received without any further purification.

2.2. Preparation of catalysts

Catalysts used in the present study namely, sulfated zirconia (S-ZrO_2), UDCaT-4, UDCaT-5, and UDCaT-6 were prepared by well established procedures in our laboratory and the details are given below.

2.2.1. Preparation of sulfated zirconia (S-ZrO_2)

Sulfated zirconia (S-ZrO_2) was prepared by adding aqueous ammonia solution to zirconium oxychloride solution at a pH of 10, as detailed elsewhere [13]. The precipitate was thoroughly washed with distilled water and made free from ammonia and chloride ions. It was dried in an oven at 120 °C for 24 h. The sulfation of the zirconia was done using 15 cm^3 g^{-1} of 0.5 M sulfuric acid. It was dried at 110 °C and calcined at 650 °C for 3 h.

2.3. Preparation of UDCaT-4

The ordered hexagonal mesoporous silica (HMS) was prepared according to our earlier work [14]. Desired quantities of zirconium oxychloride and aluminum nitrate were dissolved in aqueous solution and added to precalcined HMS by incipient wetness technique. After addition the solid was dried in an oven at 110 °C for 3 h. The dried material was hydrolyzed by ammonia gas and washed with deionized water until a neutral filtrate was obtained and the absence of chlorine ion in the filtrate was detected by phenolphthalein indicator and silver nitrate tests. It was then dried in an oven for 24 h at 110 °C. Persulfation was carried out by immersing the above solid material in to 0.5 M aqueous solution of ammonium persulfate for 30 min. It was dried at 110 °C for 24 h and calcined at 650 °C for 3 h to get active catalyst called UDCaT-4 with 0.6% (w/w) of alumina [14].

2.4. Preparation of UDCaT-5

UDCaT-5 was prepared by adding aqueous ammonia solution to zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) solution at pH of 9–10. The precipitated zirconium hydroxide so obtained was washed with deionized water until a neutral filtrate was obtained. The absence of chloride ions was detected by $AgNO_3$ test. A material balance on chloride ions before and after precipitation and washing shows no retention of Cl^- on the solid. Zirconium hydroxide ($Zr(OH)_4$) was dried in an oven for 24 h at 100 °C and was crushed to 100 mesh size. $Zr(OH)_4$ then immersed in 15 cm^3 g^{-1} of 0.5 M solution of chlorosulfonic acid and ethylene dichloride. All materials were immersed for

5 min in the solution and then without allowing moisture absorption were kept in an oven and the heating was started slowly to 120 °C after about 30 min. The solids were kept in an oven at 120 °C for 24 h and calcined at 650 °C for 3 h to get the active catalysts UDCaT-5 [15].

2.5. Preparation of UDCaT-6

UDCaT-6 was prepared by adding an aqueous solution of 2.5 g zirconium oxychloride to 5 g precalcined HMS by incipient wetness technique and it was dried in an oven at 120 °C for 3 h. The dried material was hydrolyzed by ammonia gas and washed with distilled water until no chloride ions were detected which was confirmed by the $AgNO_3$ test. It was further dried in an oven for 2 h at 120 °C. $Zr(OH)_4$/HMS was immersed in 15 $cm^3\ g^{-1}$ of 0.5 M chlorosulfonic acid in ethylene dichloride. It was soaked for 5 min in the solution and then without allowing moisture absorption, it was oven dried to evaporate the solvent at 120 °C after about 30 min. The sample was kept in an oven at 120 °C for further 24 h and calcined thereafter at 650 °C for 3 h to get the active catalyst UDCaT-6 [16].

2.6. Catalysts characterization

The catalysts, namely, UDCaT-4, UDCaT-5, UDCaT-6 and sulfated zirconia (S-ZrO_2) were completely characterized by ammonia-temperature programmed desorption (NH_3-TPD), X-ray powder diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area and Fourier transform infrared (FTIR) and the details were published by us [13–16]. Only a few salient features which are thought be important are reported here.

2.6.1. Characterization of UDCaT-4

The XRD, BET surface area and pore size analyses provided an explanation for the entrapment of nanoparticles of persulfated alumina zirconia (PAZ) (<3.6 nm) in mesoporous of HMS. The XRD of UDCaT-4 suggested that the structural integrity of HMS was maintained even after converting it into UDCaT-4. The diffractogram of UDCaT-4 further revealed that the introduction of a small amount of alumina (0.16%, w/w) and sulfate ion (1.17%, w/w) stabilized the tetragonal phase of the zirconia, which is an ideal phase conducive for superacidity in sulfated zirconia, into the pores of HMS. Furthermore, the pore volume of UDCaT-4 (0.21 $cm^3\ g^{-1}$) is much less than that of pure HMS (0.78 $cm^3\ g^{-1}$) indicating that large amount of crystalline zirconia (9.01%, w/w), and alumina must be present inside the pores of UDCaT-4. FTIR spectroscopy and energy dispersive X-ray (EDAX) analysis further support the assumption drawn on introduction of sulfate ion in UDCaT-4. The sulfur Ka_1 and zirconium La_1 distribution spectra determined by EDAX analysis show the incorporation and homogeneous distribution of zirconia and sulfur atoms in UDCaT-4. Temperature programmed desorption (TPD) profiles of PAZ and UDCaT-4 show that although UDCaT-4 possesses both weak and medium acid sites, the total number of acid sites of UDCaT-4 (0.56 $mmol\ g^{-1}$) are greater than those of PAZ (0.09 $mmol\ g^{-1}$) [14]. Scanning electron micrographs (SEM) of UDCaT-4 revealed that similar to the morphology of HMS, UDCaT-4 is made up of sub-micrometer sized free standing or aggregated sphere shaped particles. SEM analysis further supports the argument that active centers of the PAZ are successfully embedded in HMS and the structural integrity of HMS is unaltered even after it is converted to UDCaT-4 [14].

2.6.2. Characterization of UDCaT-5

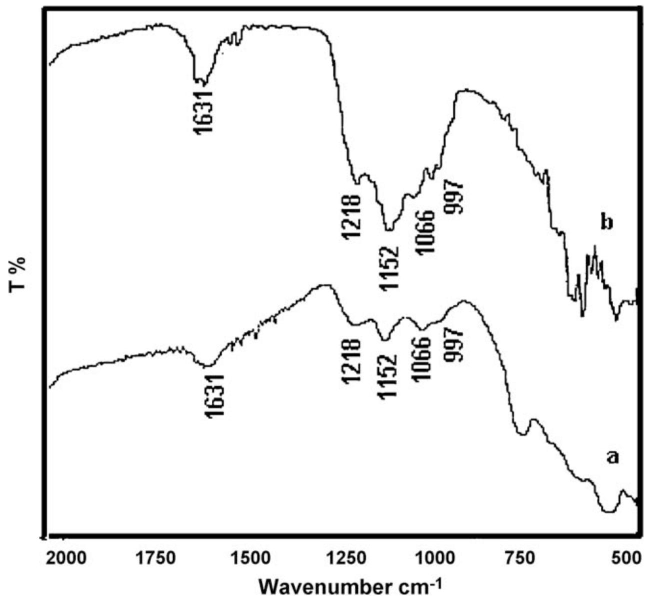


Fig. 1. FTIR spectra of (a) sulfated zirconia (S-ZrO_2) and (b) UDCaT-5.

UDCaT-5 was fully characterized by FTIR, XRD, BET surface area, NH_3-TPD, elemental analysis and the details have been published by us [15]. Ammonia-TPD was used to determine the acid strength of UDCaT-5. Ammonia-TPD analysis shows that apart from intermediate and strong acidic sites present in sulfated zirconia, UDCaT-5 also contains superacidic sites. The elemental analysis showed the complete absence of chloride species and that 9% (w/w) sulfate was retained on the surface of UDCaT-5 which was the highest then reported in the literature. The IR spectra of the S-ZrO_2 show a similar pattern as UDCaT-5 (Fig. 1) indicating the presence of the bidentate chelating sulfate group co-ordinated to zirconia [13,15]. IR spectroscopy confirms that the chlorosulfonic acid is decomposed during calcination at 650 °C and sulfate ions are retained on the surface of UDCaT-5 and thus the sulfur content is higher in UDCaT-5. Powder XRD shows the crystal structure of zirconia is not affected by a high sulfur content of 9% (w/w) in UDCaT-5. The quantity of tetragonal phase of zirconia in UDCaT-5 is the same as that in the ordinary S-ZrO_2 (Fig. 2). The XRD study proved that the tetragonal phase in the UDCaT-5 was preserved. The BET surface area of UDCaT-5 (83 $m^2\ g^{-1}$) is lower than that of S-ZrO_2 (103 $m^2\ g^{-1}$). The

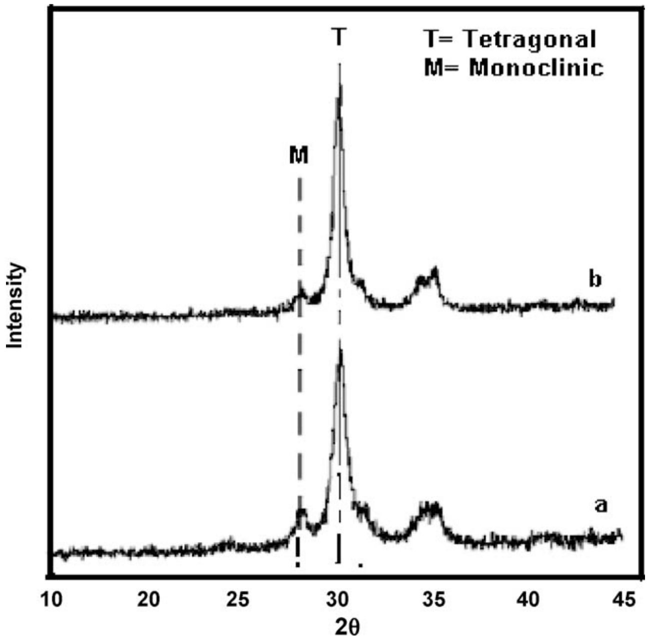


Fig. 2. XRD pattern of (a) sulfated zirconia (S-ZrO_2) and (b) UDCaT-5.

surface area of S-ZrO_2 gradually increases at low sulfate contents up to 4% (w/w) (119 $m^2 g^{-1}$) but it decreases abruptly at a maximum sulfate content of 5.64% (71 $m^2 g^{-1}$) due to the migration of sulfate ions to the bulk phase of zirconia. The surface area of UDCaT-5 decreased abruptly at the maximum sulfur content. It was due to the migration of sulfate ions from bulk phase to zirconia matrix. Thus maximum sulfur present on surface of the catalyst decreases its surface area. Thus, UDCaT-5 is superacidic in nature due to the presence of very high sulfur content present on the zirconia matrix with preservation of tetragonal phase of zirconia [15].

2.6.3. Characterization of UDCaT-6

FTIR spectroscopy and EDAX analyses support the introduction and retention of sulfate ion in UDCaT-6. XRD, BET surface area and pore size analysis provided an explanation for entrapment of nanoparticles of zirconia in mesoporous of HMS. The XRD of UDCaT-6 suggested that the structural integrity of HMS was retained even after converting it into UDCaT-6. Furthermore, the pore volume of UDCaT-6 (0.7 $cm^3 g^{-1}$) is much less than that of pure HMS (1.2 $cm^3 g^{-1}$) indicating that large amount of crystalline nanoparticles of zirconia must be present inside the pores of UDCaT-6. The sulfur $K\alpha_1$ and zirconium $L\alpha_1$ distribution spectra determined by EDAX analysis shows the incorporation and homogeneous distribution of zirconia and sulfur atoms in UDCaT-6. The SEM of UDCaT-6 revealed that similar to the morphology of HMS, UDCaT-6 is made up of sub-micrometer sized free standing or aggregated sphere shaped particle and that active centers of zirconia are successfully embedded in HMS and the structural integrity of HMS is unaltered even after it is converted to UDCaT-6 [16].

2.7. Reaction procedure

The reactions were carried out in a 100 cm^3 capacity Parr autoclave reactor with an internal diameter of 5 cm, equipped with a four bladed pitched turbine impeller. The temperature was maintained at ±1 °C of the desired value with the help of an in-built proportional integral differential (PID) controller. Specific quantities of desired reactants and catalyst were charged into the reactor and the temperature was raised to the desired value. Then, an initial sample was withdrawn and agitation started. Further samples were withdrawn at periodic time intervals up to 3 h to monitor the reaction. All catalysts were dried in an oven at 120 °C for 1 h before use. In a typical reaction, 0.376 mol toluene was reacted with 0.0752 mol propionic anhydride (PA) (5:1 mole ratio of toluene to propionic anhydride) with 3 g of catalyst; this makes the catalyst loading as 0.06 g cm^{-3} of liquid phase. The total volume of the reaction mixture was 50 cm^3. The reaction was carried out at 180 °C at a speed of agitation of 1000 rpm under autogenous pressure. The reaction was carried out without any solvent.

2.8. Analytical methods

Clear liquid samples were withdrawn at regular time intervals by reducing the speed of agitation momentarily to zero and allowing the catalyst to settle at the bottom of the reactor. Analysis of the samples or compounds were performed by Gas Chromatograph (Chemito, India: Model 8610 GC) equipped with a 10% SE-30 (liquid stationary phase) stainless steel column (3.175 mm diameter × 4 m length) with flame ionization detector (FID). Products were isolated and confirmed through gas chromatography–mass spectrometry (GC–MS) and their physical properties and retention times were recorded and compared with authentic samples. Calibrations were done with authentic samples for quantification of data. The conversions were based on the disappearance of propionic anhydride, the limiting reactant in the reaction mixture.

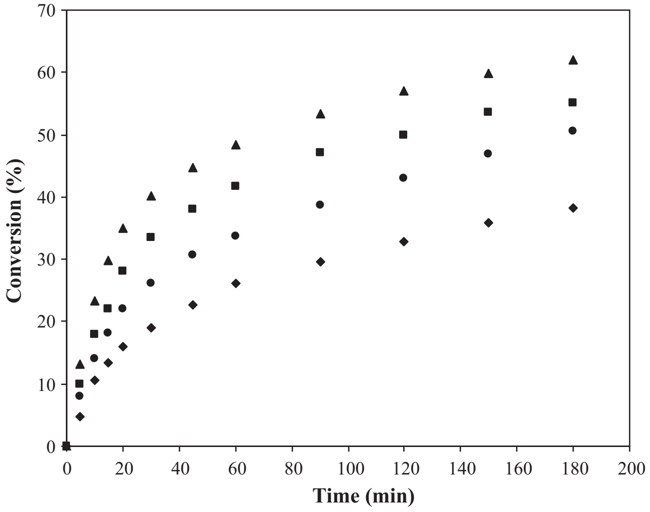


Fig. 3. Effect of different catalysts on conversion of propionic anhydride. Reaction conditions: speed of agitation = 1000 rpm, catalyst loading = 0.06 g cm^{-3}, mole ratio of toluene:propionic anhydride = 5:1, temperature = 180 °C, total reaction volume = 50 cm^3, autogenous pressure: (▲) UDCaT-5, (■) UDCaT-4, (●) UDCaT-6, (♦) sulfated zirconia (S-ZrO_2).

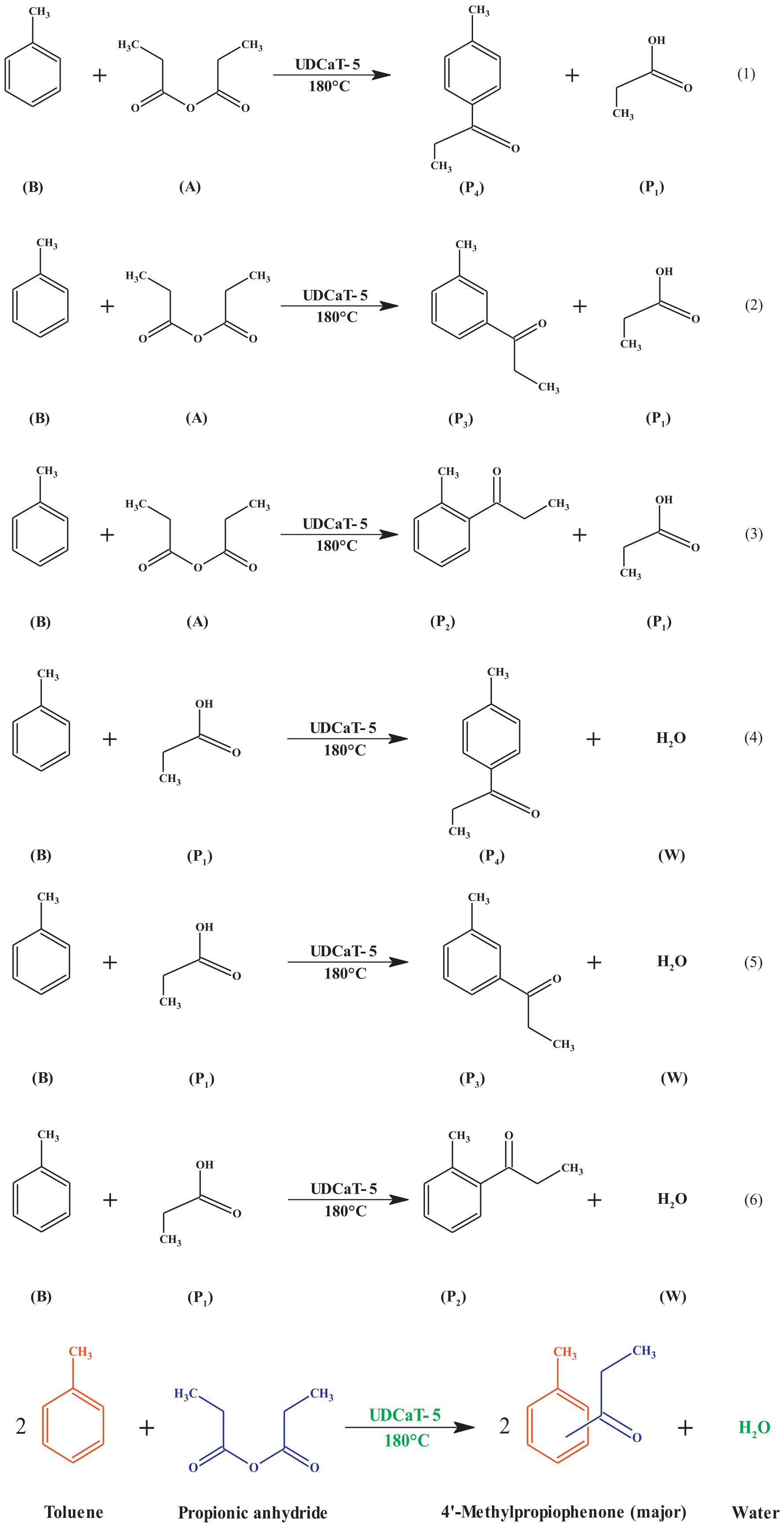
3. Results and discussions

3.1. Efficacies of various catalysts

The effects of various process parameters on conversion, rates of reaction and product distribution were studied systematically. Various parallel reactions were take place over UDCaT-5 as shown in Scheme 1. Toluene (B) and propionic anhydride (A) are chemisorbed on the acidic sites. This is a complex reaction network with parallel and consecutive reactions of toluene with propionic anhydride and propionic acid; which was in operation during the reaction process as shown in reactions (1)–(6) of Scheme 1.

Various solid superacids synthesized in our laboratory, namely, UDCaT-4, UDCaT-5, UDCaT-6 and sulfated zirconia were screened to assess their efficacy in this reaction. A 0.06 g cm^{-3} loading of the particular catalyst based on the volume of the reaction mixture was employed at 180 °C at a speed of agitation of 1000 rpm. It was found that UDCaT-5 showed higher conversion of the limiting reactant, propionic anhydride (62%) as compared to the other catalysts with selectivity (67%) towards the desired product, 4′-methylpropiophenone (4′-MPP) during 3 h of reaction and the order of activity was: UDCaT-5 (most active) > UDCaT-4 > UDCaT-6 > sulfated zirconia (S-ZrO_2) (least active) (Fig. 3). All other catalysts contain fewer acidic sites as compared to UDCaT-5 and thus the results are in this order. The purpose of using several different solid acid catalysts was to study the effect of nature, strength and distribution of acidity, pore size distribution and stability of the catalyst on conversion and selectivity in a complex network of reactions involving acylation and dehydration. Since the substrate is bulky and involves generation of water, it is essential that sulfated zirconia which gets deactivated is modified. Besides, our group was the first one to report the highest superacidity in solid superacids. This has been already published by us [15]. The catalyst properties, selectivity of 4′-MPP and final conversion of propionic anhydride are given in Table 1, which clearly indicates that UDCaT-5 is the most active and selective catalyst in terms of conversion and selectivity.

Propionic acid, which is formed during the reaction course (Scheme 1) reacts further with toluene to produce 4′-MPP and generates water. This was also verified by doing an independent experiment with toluene (excess) and propionic acid (limiting) to



Scheme 1. Friedel–Crafts acylation of toluene with propionic anhydride over UDCaT-5. Where, A = propionic anhydride, B = toluene, P_1 = propionic acid, P_2 = 2′-methylpropiophenone (2′-MPP), P_3 = 3′-methylpropiophenone (3′-MPP), P_4 = 4′-methylpropiophenone (4′-MPP), W = water.

Table 1
Properties of catalysts and conversion of propionic anhydride.[a]

Catalyst	Source	Average pore diameter (Å)	Surface area ($m^2\,g^{-1}$)	Acidity by NH_3-TPD ($mmol\,g^{-1}$)	Selectivity of 4′-MPP after 3 h (%)	Conversion of propionic anhydride after 3 h (%)
UDCaT-4	This work	30	233	0.562	52	55
UDCaT-5	This work	40	83	0.584	67	62
UDCaT-6	This work	32	877	0.508	56	51
Sulfated zirconia (S-ZrO_2)	This work	40	100	0.433	43	38

[a] Reaction conditions: speed of agitation = 1000 rpm, catalyst loading = 0.06 g cm^{-3}, mole ratio of toluene:propionic anhydride = 5:1, temperature = 180 °C, total reaction volume = 50 cm^3, autogenous pressure.

observe that the reaction indeed took place. Novel mesoporous solid superacid catalyst UDCaT-5 showed the highest activity comparing to other catalysts even in the presence of water as a co-product of this reaction. Hence further experiments were conducted with UDCaT-5. The concentration profile of reactants and the products at 180 °C are shown in Fig. 4. Concentration of propionic anhydride decreases gradually, whereas the concentration of 4′-MPP increases sharply due to the consumption of toluene and propionic anhydride during the reaction. Even at this condition, the concentration of 2′-methylpropiophenone (2′-MPP) and 3′-methylpropiophenone (3′-MPP) increases slightly up to certain limits. The scenario also shows that during reaction, the concentration of propionic acid increases suddenly up to 20 min and then drops gradually toward zero. This supports the above discussion of formation and consumption of propionic acid during the reaction. Indeed, carboxylic acids are good acylating agents with strong solid acids [4].

3.2. Green metrics of the process

The green metrics of this process are presented in Table 2. Typically in acylation reactions; carboxylic acid anhydrides are used, which lead to the formation of ketone and corresponding carboxylic acid. Thus, the carboxylic acid has to be recovered. Depending on the type of anhydride, the carboxylic acid loss is significant. In the current case, the expected product of reaction is given by reaction (1). On the contrary because of the superacidity of UDCaT-5 used here, a second reaction with propionic acid takes place (reaction (4)) for 4′-methylpropiophenone. Toluene ($MW = 92.14\,g\,mol^{-1}$) reacts with priopionic anhydride ($MW = 130.14\,g\,mol^{-1}$) to produce 4′-methylpropiophenone ($MW = 148.2\,g\,mol^{-1}$) and propionic acid ($MW = 74.08\,g\,mol^{-1}$) which further reacts to give the product and water. Thus, in this case, 2 mol of toluene reacts with 1 mol of priopionic anhydride giving 2 mol of product and 1 mole of water (Scheme 1). In other words, in this reaction, $\{(2 \times 148.2)/(2 \times 92.14 + 130.14)\} \times 100 = 94.26\%$ atoms are incorporated in the monoacylated product. All three products 2′, 3′ and 4′-methylpropiophenone are useful intermediates and can be separated. Thus, in this process atom efficiency is achieved. Indeed, because of the superacidic nature of the catalyst; waste is reduced. The other green parameters are given in Table 2 [18–21].

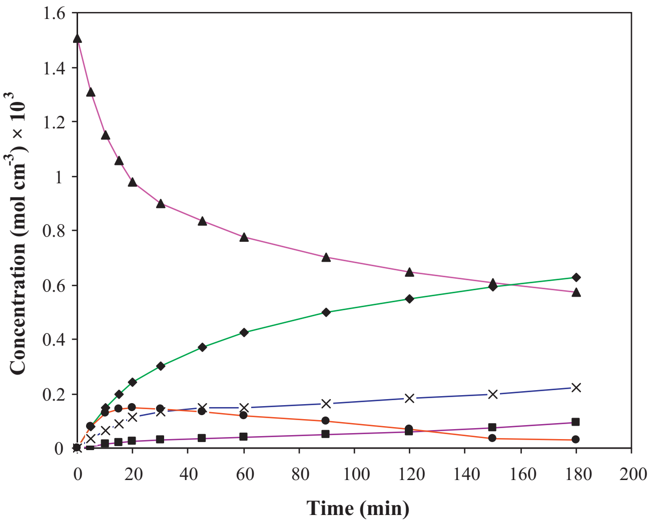


Fig. 4. Concentration profile of various products in acylation of toluene with propionic anhydride. Reaction conditions: catalyst = UDCaT-5, speed of agitation = 1000 rpm, catalyst loading = 0.06 g cm^{-3}, mole ratio of toluene:propionic anhydride = 5:1, temperature = 180 °C, total reaction volume = 50 cm^3, autogenous pressure: (▲) propionic anhydride, (◆) 4′-MPP, (■) 3′-MPP, (×) 2′-MPP, (●) propionic acid.

3.3. Effect of speed of agitation

The effect of speed of agitation was studied in the range of 800–1200 rpm at a catalyst loading 0.06 g cm^{-3} at 180 °C (Fig. 5). The mole ratio of toluene to propionic anhydride was kept 5:1. There was no significant change in the rate and conversion patterns, which was indicative of the absence of any resistance to external mass transfer of propionic anhydride to the external surface of the catalysts. However, all further reactions were carried out at a speed of 1000 rpm. We have given the theoretical development in some of our earlier work [9]. Theoretical calculations were also done to establish that there was absence of external mass transfer

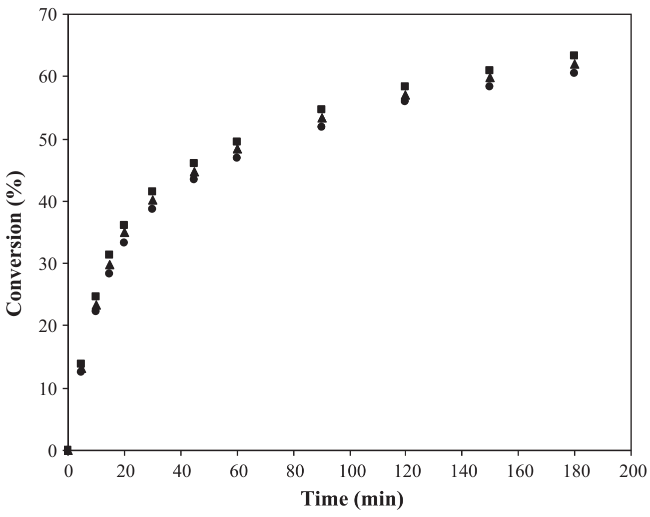


Fig. 5. Effect of speed of agitation on conversion of propionic anhydride. Reaction conditions: catalyst = UDCaT-5, catalyst loading = 0.06 g cm^{-3}, mole ratio of toluene:propionic anhydride = 5:1, temperature = 180 °C, total reaction volume = 50 cm^3, autogenous pressure: (●) 800 rpm, (▲) 1000 rpm, (■) 1200 rpm.

Table 2
Green metrics for the current work.

Atom economy for monoacylation	$\frac{\text{MW of product}}{\text{MW of all reactants used in reaction}} \times 100$	94.26%
Conversion of propionic anhydride (limiting reactant)	$\left(1 - \frac{\text{Final mol of limiting reactant}}{\text{Initial mol of limiting reactant}}\right) \times 100$	62%
Selectivity of 4′-methylpropiophenone	$\frac{\text{Final mol of 4}'\text{-methylpropiophenone}}{\text{Total mol of all products}} \times 100$	67%
Yield of 4′-methylpropiophenone	$\frac{\text{Final mol of 4}'\text{-methylpropiophenone}}{\text{Initial mol of propionic anhydride}} \times 100$	41.54%
Atom economy of 4′-methylpropiophenone	$\frac{\text{MW of product}}{\text{MW of all reactants used in reaction}} \times 100$	63.15%
Reaction mass efficiency (RME)	$\frac{\text{Mass of isolated products}}{\text{Total mass of reactants used in reaction}} \times 100$	20.77%
Carbon efficiency of monoacylated products	$\frac{\text{Mass of carbon in monoacylated products}}{\text{Total mass of carbon in key reactants}} \times 100$	100%
Carbon efficiency of 4′-methylpropiophenone	$\frac{\text{Mass of carbon product}}{\text{Total mass of carbon in key reactants}} \times 100$	67%
E factor (monoacylation)	$\frac{\text{Mass of waste}}{\text{Mass of product}}$	0.06

NB: All ketones are useful products and can be separated. The selectivity to 4′-methylpropiophenone is considered. There was only monoacylation and water is the only co-product of the overall reaction.

resistance. It confirms that the mass transfer rates were much higher than rates of reaction and hence speed of agitation had no influence on reaction rate.

3.4. *Effect of catalyst loading*

The effect of catalyst loading was studied over range of 0.01–0.07 g cm^{-3} (Fig. 6). The initial rates of reaction, in the absence of external mass transfer resistance, are plotted against catalyst loading in Fig. 7. It demonstrates that the rates are directly proportional to the catalyst loading based on the entire liquid phase volume. This indicates that, as the catalyst loading increased, the conversion of propionic anhydride increases, which is due to proportional increase in the number of active sites of catalyst. There was only a little higher conversion of propionic anhydride in case of 0.07 g cm^{-3} catalyst loading than that of 0.06 g cm^{-3} (Fig. 6); even in this case the rate of reaction was almost constant between 0.06 g cm^{-3} and 0.07 g cm^{-3} catalyst loading (Fig. 7). This suggests that the number of sites available were more than required and hence all further reactions were carried out with 0.06 g cm^{-3} catalyst loading as used in the

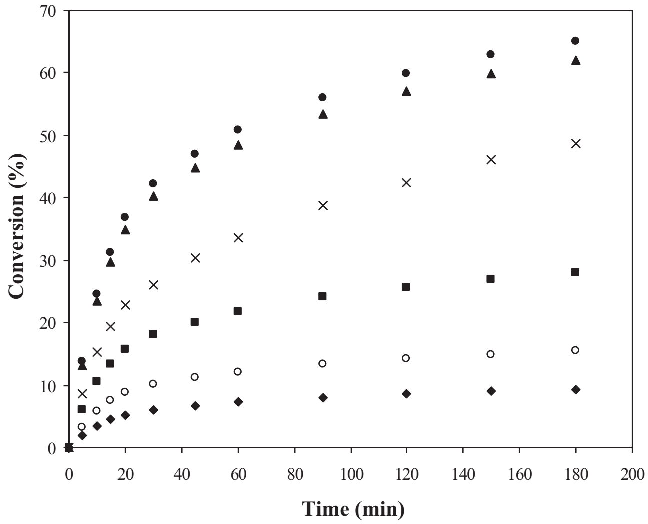


Fig. 6. Effect of catalyst loading on conversion of propionic anhydride. Reaction conditions: catalyst = UDCaT-5, speed of agitation = 1000 rpm, mole ratio of toluene:propionic anhydride = 5:1, temperature = 180 °C, total reaction volume = 50 cm^3, autogenous pressure: (◆) 0.01 g cm^{-3}, (○) 0.02 g cm^{-3}, (■) 0.04 g cm^{-3}, (×) 0.05 g cm^{-3}, (▲) 0.06 g cm^{-3}, (●) 0.07 g cm^{-3}.

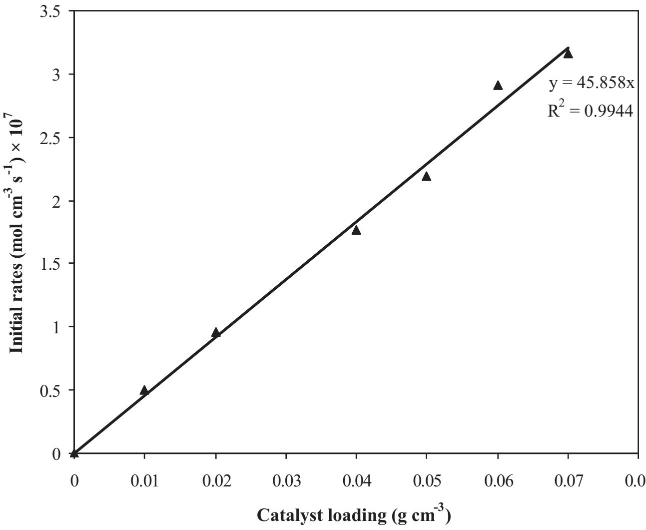


Fig. 7. Plot of initial rate of reaction as a function of catalyst loading in liquid phase. Reaction conditions: catalyst = UDCaT-5, speed of agitation = 1000 rpm, mole ratio of toluene:propionic anhydride = 5:1, temperature = 180 °C, total reaction volume = 50 cm^3, autogenous pressure.

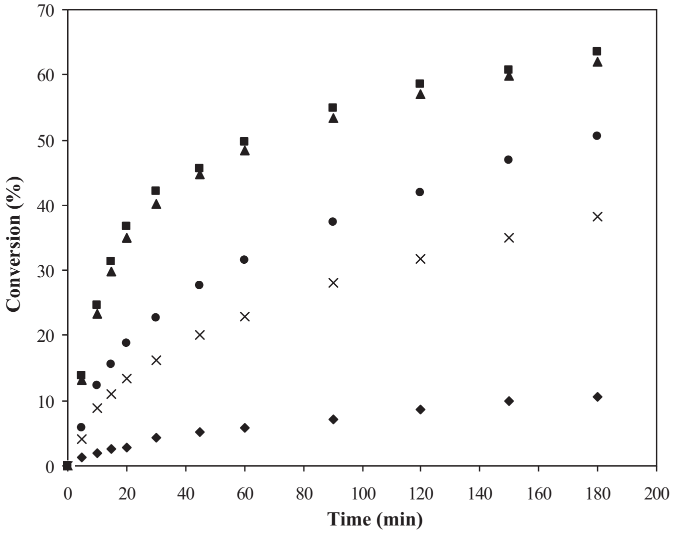


Fig. 8. Effect of mole ratio of toluene:propionic anhydride on conversion of propionic anhydride. Reaction conditions: catalyst = UDCaT-5, speed of agitation = 1000 rpm, catalyst loading = 0.06 g cm^{-3}, temperature = 180 °C, total reaction volume = 50 cm^{3}, autogenous pressure: (◆) 1:1, (×) 3:1, (●) 4:1, (▲) 5:1, (■) 6:1.

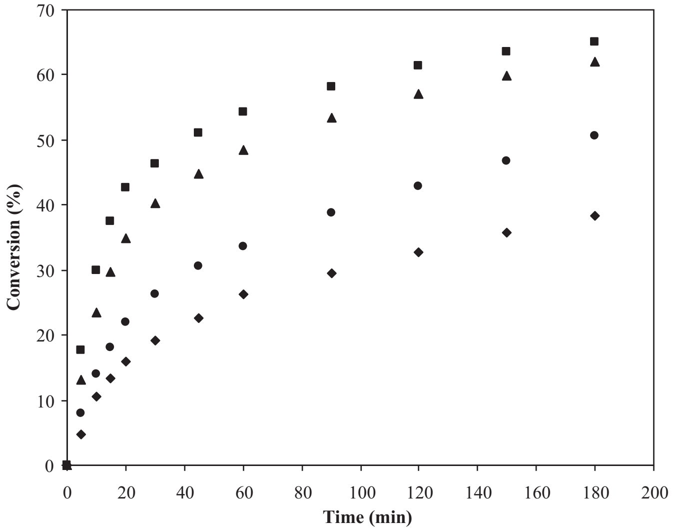


Fig. 9. Effect of temperature on conversion of propionic anhydride. Reaction conditions: catalyst = UDCaT-5, speed of agitation = 1000 rpm, catalyst loading = 0.06 g cm^{-3}, mole ratio of toluene:propionic anhydride = 5:1, total reaction volume = 50 cm^{3}, autogenous pressure: (◆) 160 °C, (●) 170 °C, (▲) 180 °C, (■) 190 °C.

standard reaction. At this loading, the intraparticle diffusion resistance sets in.

3.5. *Proof of absence of intraparticle resistance*

The average particle size of UDCaT-5 was found to be in the range of 40–50 μm. The catalyst is amorphous in nature; so it was not possible to study the effect of catalyst particle size on the rate of reaction. The average particle diameter of UDCaT-5 used in the reactions was 0.0045 cm. Therefore, a theoretical calculation was done based on the Weisz-Prater criterion [22,23] to assess the influence of intraparticle diffusion resistance. According to the Weisz-Prater criterion, the value of $\{-r_{obs}\rho_p R_p{}^2/D_e[A_s]\}$ has to be much less than unity for the reaction to be intrinsically kinetically controlled; which represents the ratio of the intrinsic reaction rate to the intraparticle diffusion rate. This can be evaluated from the observed rate of reaction ($-r_{obs} = 4.86 \times 10^{-6}$ mol gcat^{-1} s^{-1}), density of catalyst particle ($\rho_p = 1.255$ g cm^{-3}), the particle radius ($R_p = 2.25 \times 10^{-3}$ cm), the effective diffusivity of the limiting reactant ($D_e = 1.549 \times 10^{-4}$ cm^2 s^{-1}), and the concentration of the reactant at the external surface of the particle ($[A_s] = 1.51 \times 10^{-3}$ mol cm^{-3}). The calculated value of 1.32×10^{-4} is less than unity, which further reveals that the absence of intraparticle diffusion resistance at the reaction conditions. A further proof of the absence of the intraparticle diffusion resistance was obtained through the study of the effect of temperature as discussed later.

3.6. *Effect of mole ratio*

The effect of toluene to propionic anhydride mole ratio was studied at 1:1 to 6:1 by keeping the catalyst loading constant. The conversion of propionic anhydride was found to increase with an increase in concentration of toluene (Fig. 8). Beyond a mole ratio 5:1 there was no significant difference between the conversion levels of propionic anhydride. Therefore, all further reactions having been studied by using a toluene to propionic anhydride mole ratio of 5:1.

3.7. *Effect of temperature*

After the external mass transfer and intra-particle diffusion limitations were eliminated, the effect of temperature on conversion of propionic anhydride was studied under otherwise similar conditions at 160, 170, 180 and 190 °C, respectively. It was observed that the conversion of propionic anhydride increased with temperature (Fig. 9). This would suggest an intrinsically kinetically controlled mechanism which shows significant increase in the conversion profile with temperature. With an increase in temperature, both the rate of reaction as well as selectivity for 4′-MPP increased. There is no significant difference in the final conversion of propionic anhydride between 180 °C (62%) and 190 °C (65%), and also the selectivity for 4′-MPP was 67% at 180 °C and 69% at 190 °C after 3 h of the reaction course. Therefore, 180 °C is the optimum temperature for this reaction.

3.8. *Reusability of catalyst*

The stability of the active species in solution has been of concern for solid acids, since UDCaT-5 showed the best results, the reusability studies were performed by employing them in a model reaction. The model reaction was carried out by using 3 g of catalyst and the experiments were properly scaled up. The catalyst reusability was studied three times, including the use of fresh catalyst. After each run the catalyst was filtered, and then refluxed with 50 cm^3 methanol for 1 h in order to remove any adsorbed material from catalyst surface within pores. The catalyst was then dried at 120 °C for 3 h and weighed before using in the next batch. The actual amount of catalyst used in the next batch, was almost 5% less than the previous batch. There was some attrition of catalyst particle during agitation. In a typical batch reaction, there were inevitably losses of particles during filtration due to attrition. Although the catalyst was washed after filtration to remove all adsorbed reactants and products, there was still a possibility of retention of small amount of adsorbed reactants and products species which might cause the blockage of active sites of the catalyst and loss in yield on successive runs. These are apparent factors for the loss in activity, which have been taken into account because no fresh catalyst was added into the reaction mixture to maintain the same catalyst loading during reusability tests. But this catalyst could be recovered

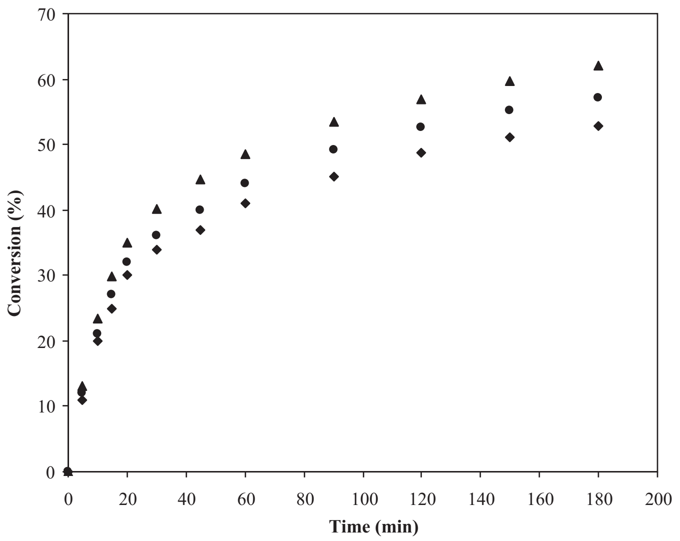


Fig. 10. Reusability of catalyst. Reaction conditions: catalyst = UDCaT-5, speed of agitation = 1000 rpm, catalyst loading = 0.06 g cm^{-3}, mole ratio of toluene:propionic anhydride = 5:1, temperature = 180 °C, total reaction volume = 50 cm^{3}, autogenous pressure: (▲) fresh catalyst, (●) first reuse, (♦) second reuse.

and subsequently reused several times in a solventless system. It showed no significant loss of activity after three successive runs. It was observed that there was only a marginal decrease in conversion (Fig. 10) and there was no effect on selectivity of the products. When make-up quantity of the catalyst was added, almost similar conversions were found to suggest that the catalyst was stable and reusable.

3.9. *Reaction kinetics*

The above results were used to build a kinetic model. The reaction involves two organic phase reactants, limiting reactant A (propionic anhydride), excess reactant B (toluene); the desired product P_4 (4′-methylpropiophenone) and co-product P_1 (propionic acid). Since A and B are liquid phase reactants, they need to diffuse to the interior surface of the catalyst.

Various parallel as well as consecutive reactions take place over UDCaT-5 as shown in Scheme 1. Toluene (B) and propionic anhydride (A) are chemisorbed on the acidic sites. This is a complex reaction network with parallel reaction of toluene with propionic anhydride and consecutive reactions of toluene with propionic acid (which was produced during the reaction process) take place as shown in reactions (1)–(6) of Scheme 1. The Langmuir–Hinshelwood–Hougen–Watson (LHHW) type of kinetic model will result into a Power Law model; if the adsorption of all species is weak [24]. The different reaction steps involved in this process are according to the Power Law model, which was found to hold for acid catalyzed reactions. For a fixed catalyst loading (w), the rates of reaction or formation can be established. The following reaction steps occurred over UDCaT-5:

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_1} \mathrm{P}_4 + \mathrm{P}_1 \tag{1}$$

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_2} \mathrm{P}_3 + \mathrm{P}_1 \tag{2}$$

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_3} \mathrm{P}_2 + \mathrm{P}_1 \tag{3}$$

$$\mathrm{P}_1 + \mathrm{B} \xrightarrow{k_4} \mathrm{P}_4 + \mathrm{W} \tag{4}$$

$$\mathrm{P}_1 + \mathrm{B} \xrightarrow{k_5} \mathrm{P}_3 + \mathrm{W} \tag{5}$$

$$\mathrm{P}_1 + \mathrm{B} \xrightarrow{k_6} \mathrm{P}_2 + \mathrm{W} \tag{6}$$

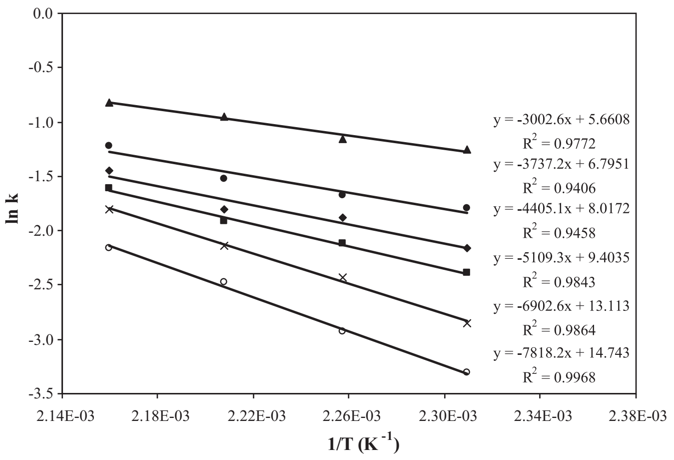


Fig. 11. Arrhenius plots. (▲) reaction (1), (■) reaction (2), (●) reaction (3), (♦) reaction (4), (○) reaction (5), (×) reaction (6).

where, A = propionic anhydride, B = toluene, P_1 = propionic acid, P_2 = 2′-methylpropiophenone (2′-MPP), P_3 = 3′-methylpropiophenone (3′-MPP), P_4 = 4′-methylpropiophenone (4′-MPP), W = water, and k_1, k_2, k_3, k_4, k_5, k_6 are the rate constants of respective reactions.

The net rate of consumption of propionic anhydride (A) by three parallel reactions (Eqs. (1)–(3)) is given by:

$$-r_{\mathrm{A}} = -\frac{dC_{\mathrm{A}}}{dt} = k_1 w C_{\mathrm{A}} C_{\mathrm{B}} + k_2 w C_{\mathrm{A}} C_{\mathrm{B}} + k_3 w C_{\mathrm{A}} C_{\mathrm{B}}$$
$$= (k_1 + k_2 + k_3) w C_{\mathrm{A}} C_{\mathrm{B}} \tag{7}$$

The rate of reaction of propionic anhydride ($-r_{\mathrm{A}}$) is in mol cm^{-3} s^{-1}, the concentrations in mol cm^{-3}, the second order rate constant in cm^6 gcat^{-1} mol^{-1} s^{-1} and catalyst loading (w) in g cm^{-3}. Similarly, the net rate of consumption of toluene ($-r_{\mathrm{B}}$) and the net rate of formations of propionic acid (r_{P_1}), 2′-methylpropiophenone (r_{P_2}), 3′-methylpropiophenone (r_{P_3}), 4′-methylpropiophenone (r_{P_4}) and water (r_{W}) are as follows:

$$-r_{\mathrm{B}} = -\frac{dC_{\mathrm{B}}}{dt} = (k_1 + k_2 + k_3) w C_{\mathrm{A}} C_{\mathrm{B}} + (k_4 + k_5 + k_6) w C_{\mathrm{B}} C_{\mathrm{P}_1} \tag{8}$$

$$r_{\mathrm{P}_4} = \frac{dC_{\mathrm{P}_4}}{dt} = k_1 w C_{\mathrm{A}} C_{\mathrm{B}} + k_4 w C_{\mathrm{B}} C_{\mathrm{P}_1} \tag{9}$$

$$r_{\mathrm{P}_3} = \frac{dC_{\mathrm{P}_3}}{dt} = k_2 w C_{\mathrm{A}} C_{\mathrm{B}} + k_5 w C_{\mathrm{B}} C_{\mathrm{P}_1} \tag{10}$$

$$r_{\mathrm{P}_2} = \frac{dC_{\mathrm{P}_2}}{dt} = k_3 w C_{\mathrm{A}} C_{\mathrm{B}} + k_6 w C_{\mathrm{B}} C_{\mathrm{P}_1} \tag{11}$$

$$r_{\mathrm{P}_1} = \frac{dC_{\mathrm{P}_1}}{dt} = (k_1 + k_2 + k_3) w C_{\mathrm{A}} C_{\mathrm{B}} - (k_4 + k_5 + k_6) w C_{\mathrm{B}} C_{\mathrm{P}_1} \tag{12}$$

$$r_{\mathrm{W}} = \frac{dC_{\mathrm{W}}}{dt} = (k_4 + k_5 + k_6) w C_{\mathrm{B}} C_{\mathrm{P}_1} \tag{13}$$

From the knowledge of concentration profiles (Fig. 4), the individual reaction rate constants could be calculated. Mathcad or Polymath package was used to extract the rate constants (Table 3). The values of rate constant or initial rate at different temperatures were used to estimate the frequency factor (k_0) and apparent activation energy (E) of each reaction by making Arrhenius plots (Fig. 11) and are tabulated in Table 3. The values of rate constant and activation energy of all six reactions suggest that reaction 1 is faster as compared to other reactions and the rates of all six reactions are in the following order: reaction (1) (fast reaction) > reaction (3) > reaction (4) > reaction (2) > reaction (6) > reaction (5) (slow

Table 3
Kinetic parameters of various reactions.

Reaction number	Reaction[a]	Rate constant, k at 180 °C ($\mathrm{cm^6\,gcat^{-1}\,mol^{-1}\,s^{-1}}$)	Frequency factor, k_0 ($\mathrm{cm^6\,gcat^{-1}\,mol^{-1}\,s^{-1}}$)	Activation energy, E ($\mathrm{kcal\,mol^{-1}}$)
1	$A + B \xrightarrow{k_1} P_4 + P_1$	0.386	2.87×10^2	5.97
2	$A + B \xrightarrow{k_2} P_3 + P_1$	0.148	1.21×10^4	10.15
3	$A + B \xrightarrow{k_3} P_2 + P_1$	0.219	8.93×10^2	7.43
4	$P_1 + B \xrightarrow{k_4} P_4 + W$	0.165	3.03×10^3	8.75
5	$P_1 + B \xrightarrow{k_5} P_3 + W$	0.084	2.53×10^6	15.53
6	$P_1 + B \xrightarrow{k_6} P_2 + W$	0.118	4.95×10^5	13.72

[a] Where, A = propionic anhydride, B = toluene, P_1 = propionic acid, P_2 = 2′-methylpropiophenone (2′-MPP), P_3 = 3′-methylpropiophenone (3′-MPP), P_4 = 4′-methylpropiophenone (4′-MPP), W = water, and k_1, k_2, k_3, k_4, k_5, k_6 are the rate constants of respective reactions.

reaction). This also indicates that acylation of toluene with propionic anhydride is the faster reaction than acylation of toluene with propionic acid (Table 3). The values of activation energy also supported the fact that the overall rate of reaction is not influenced by either external mass transfer or intraparticle diffusion resistance and it is an intrinsically kinetically controlled reaction on active sites of the catalyst.

4. Conclusion

Friedel–Crafts acylation of toluene with propionic anhydride to synthesise 4′-methylpropiophenone was studied at 180 °C over variety of ecofriendly solid acid catalysts such as UDCaT-4, UDCaT-5, UDCaT-6 and sulfated zirconia. UDCaT-5 was found to be the most active, selective, stable and reusable catalyst. The effect of various operating parameters on conversion, rates of reaction and product distribution over UDCaT-5 were discussed systematically. The rate of reaction increased with temperature, catalyst loading and toluene to propionic anhydride mole ratio. A kinetic model for the reaction mechanism was successfully developed and it follows Power Law model, whereby toluene and propionic anhydride are weakly adsorbed on the surface of the catalyst particle. The co-product propionic acid generated *in situ* also reacts with toluene. Water is the only co-product of the overall reaction. The values of activation energy also supported the fact that the overall rate of reaction is not influenced by either external mass transfer or intraparticle diffusion resistance and it is an intrinsically kinetically controlled reaction on active sites of the catalysts. The reaction is completely solvent free; hence leads to minimizing the waste and hazards, which could be advantageous as a green and clean method for the synthesis of 4′-methylpropiophenone.

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