

Benzoylation of toluene with *p*-toluoyl chloride over triflic acid functionalized mesoporous Zr-TMS catalyst

Shainaz M. Landge, M. Chidambaram, A.P. Singh*

Catalysis Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India

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Abstract

The catalytic liquid phase benzoylation of toluene (Tol) to 4,4'-dimethylbenzophenone (4,4'-DMBP) with *para*-toluoyl chloride (*p*-T-Cl) has been studied in a batch reactor at atmospheric pressure in the presence of different loadings of triflic acid (TFA) functionalized on the walls of mesoporous Zr-TMS (f-Zr-TMS/Zr-TMS-O-SO₂-CF₃/mesoporous ≡Zr-O-SO₂-CF₃) catalysts. Conventional catalysts, CF₃SO₃H and Zr-TMS (zirconium oxide with a mesostructured framework; TMS is transition metal oxide mesoporous molecular sieves) are also included for comparison. Under identical reaction conditions, f-Zr-TMS is considerably more active than Zr-TMS, whereas CF₃SO₃H shows higher activity. The conversion of *p*-T-Cl, rate of *p*-T-Cl conversion (turn over frequency (TOF)), selectivity to 4,4'-DMBP and 4,4'-DMBP/2,4'-DMBP ratio over f-Zr-TMS-15, after 8 h of reaction time and at 403 K are ca. 50.7%, 14.5 (10⁻¹ h⁻¹ mol⁻¹ S), 73.5% and 3.2, respectively. Acidity and mesoporosity of the f-Zr-TMS catalyst play an important role in the conversion of *p*-T-Cl, rate of *p*-T-Cl conversion and product distribution. The effect of various parameters such as duration of run, reaction time, catalyst concentration, reaction temperature, Tol/*p*-T-Cl molar ratio and re-use of catalyst, on the catalyst performance is examined in order to optimize the conversion of *p*-T-Cl and selectivity to 4,4'-DMBP. The conversion of *p*-T-Cl using f-Zr-TMS-15 is increased significantly with the increases in reaction time, catalyst concentration, reaction temperature and Tol/*p*-T-Cl molar ratio. f-Zr-TMS-15 catalyst is recycled one time (fresh + one cycle) and a decrease in *p*-T-Cl conversion is observed after one cycle, which is related to the minor leaching of anchored CF₃SO₃H by HCl (formed during reaction). © 2004 Elsevier B.V. All rights reserved.

Keywords: Benzoylation of toluene; 4,4'-Dimethylbenzophenone; f-Zr-TMS; Triflic acid

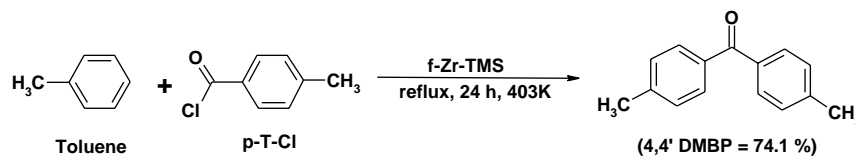
1. Introduction

4,4'-Dimethylbenzophenone (BMBP) (Di-*p*-toluoyl ketone) is used mainly as a photosensitizer and applied to the UV-curable coatings and inks. Disubstituted diphenylketones are also used as intermediates for pharmaceutical and agricultural chemicals [1]. It gives high whiteness background and high d. images showing good resistance to plasticizers [2]. Also, 4,4'-DMBP is extensively used as UV light stabilizers in plastics, cosmetics (as fixative in perfumes) and films [3]. The primary function is to protect the long-term degradation from all forms of wavelength of light and also helps in absorbing the UV radiation and prevents the formation of free radicals [4]. 4,4'-DMBP is usually synthesized by the Friedel-Crafts reaction of toluene with phosgene as an acylating agent using AlCl₃ as catalyst, resulting

in lower yield of 4,4'-DMBP [5–7]. It is also been produced by reacting toluene with oxalyl-chloride as an acylating agent and AlCl₃ as a catalyst with yield of only 55% along with 33% of *p*-toluic acid as a side product [8]. Other process includes the preparation of 4,4'-DMBP by transcarybonylation reaction in which acylation of toluene with *p*-toluic acid in presence of polyphosphoric acid (PPA) as a catalyst gives 4% yield [9]. Also, oxidation of Di-*p*-toluoyl methane with chromic acid in presence of acetic acid leads to the formation of Di-*p*-toluoyl ketone along with *p*-toluic acid as a side product, with comparable low yield of 4,4'-DMBP [10]. Again, oxidation of *p*, *p'*-dimethyldiphenylmethane in presence of copper naphthenate yields 4,4'-DMBP. [11]. Recently, 4,4'-DMBP is prepared by reacting *p*-toluic acid, toluene and various metal (praseodymium, dysprosium, indium, bismuth, cerium, thorium, scandium and yttrium) triflate catalysts; the yield of 4,4'-DMBP obtained was in the range of 4–30% [12]. Several homogenous acidic catalysts (Al₃Cl₃, TiCl₄, FeCl₃, SnCl₄, BF₃, HF, CF₃SO₃H,

* Corresponding author. Fax: +91-20-5893761.

E-mail address: apsingh@cata.ncl.res.in (A.P. Singh).



Scheme 1.

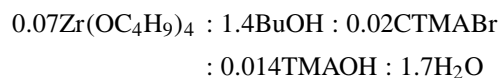
FSO₃H, and H₂SO₄) have been widely used for the acylation reactions [13–17]. However, the above used catalyst have several disadvantages; wasting a lot of homogeneous catalyst, because the reaction being mainly equimolar and of the difficulty of recycling it after use, and corrosion of containers by evolved acidic gases [18]. Some catalysts are toxic. In addition, halides of aluminium, being strong Lewis acid also, catalyze other undesirable reactions such as isomerization and *trans*-alkylation reactions [19]. Also, they tend to give less yield of 4,4'-DMBP. In order to overcome these difficulties, solid acid catalyst such as Nafion-H [20], clay [21], heteropoly acids [22], metal oxides promoted by sulphate ions (SO₄²⁻/Al₂O₃, SO₄²⁻/ZrO₂, SO₄²⁻/TiO₂, FeSO₄ and Fe₂(SO₄)₃, SO₄/SnO₂, SO₄/Al₂O₃, SO₄/HfO₂, SO₄/Fe₂O₃) [22–25]. But these catalysts have non-shape selective nature and insufficient acidity in some cases. Zirconium oxide is of particular interest because it contains both acidic and basic surface sites. Also, zirconia has a high melting point, low thermal conductivity, high corrosion resistance, and amphoteric behavior, all of which can be useful properties for a support material. The possibility of obtaining such materials with a mesoporous texture has made this oxide even more interesting [26]. “Triflic acid is known to be a ‘strong’ acid”. It is widely used in many organic reactions. However, the recovery of the triflic acid from the reaction mixture results in the formation of large amounts of waste, which is environmentally unacceptable. The desire to perform acid-catalyzed reactions over solids has resulted in new research in this area and supported triflic acid is now becoming available to replace homogeneous acid solutions [27–29]. CF₃SO₃H and its conjugate base have extremely high thermal stability and resistance to both reductive and oxidative cleavages. In addition, the use of triflates or triflic acid as homogeneous acid catalysts has received attention because of the electron-withdrawing effect exerted by the trifluoromethanesulfonyl group. Hence, the triflic acid functionalized Zr-TMS (f-Zr-TMS) was chosen to meet all the requirements for acid catalyzed reactions. f-Zr-TMS is highly acidic, thermally stable and environment friendly material [30,31]. In this paper we disclose the report for the first time of our studies on the catalytic activity of a environmentally friendly, acidic, stable and recyclable f-Zr-TMS catalyst in the benzoylation of toluene with *p*-T-Cl at atmospheric pressure (Scheme 1). Herein, we also report the influence of different wt.% loading of triflic acid on Zr-TMS, duration of run, reaction time, catalyst concentration, reaction temperature, molar ratios of reactants and reuse of the catalyst (f-Zr-TMS) on the conversion

of *p*-T-Cl and selectivity to 4,4'-DMBP. The results obtained over triflic acid functionalized mesoporous Zr-TMS catalyst are compared with CF₃SO₃H, and Zr-TMS.

2. Experimental

2.1. Synthesis of Zr-TMS

The synthesis of Zr-TMS was carried out using the following gel composition and procedure:



A mixture of zirconium(IV) butoxide and 1-butanol was stirred for 10 min. Then, the required amount of water was added dropwise into this mixture under stirring to hydrolyze the zirconium(IV) butoxide to Zr(OH)₄. Further, the precipitated Zr(OH)₄ mixture was added to aqueous solution of *N*-cetyl-*N,N,N* trimethyl ammonium bromide (CTMABr) and tetra methyl ammonium hydroxide (TMAOH) under continuous stirring. After further stirring for 2 h, the resulting synthesis gel (pH 10.5–11.0) was transferred to a round bottom flask and refluxed at 363 K for 48 h under stirring. The solid product was obtained by filtration, washed with de-ionized water and acetone, and dried at 373 K for 2 h. The surfactant from the synthesized material was removed by the extraction with a mixture containing 100 g of ethanol and 2.5 g of HCl (36 wt.%) per gram of the solid material under reflux condition for 48 h. Thus the Zr-TMS was washed with water and acetone and dried at 373 K for 2 h.

2.2. Synthesis of f-Zr-TMS

The resulting solid mesoporous material, Zr-TMS, was functionalized with triflic acid by post synthesis procedure [30,31].

Triflic acid (30 wt.%) was added dropwise into the mixture of toluene and Zr-TMS at 363 K under nitrogen atmosphere and further it was refluxed for 2 h. Then, the mixture was cooled, filtered, washed with acetone and dried at 373 K for 6 h. The Soxhlet extraction of the material was carried out at 348 K for 24 h using a mixture of dichloromethane (100 g) and diethyl ether (100 g) per gram of the catalyst. Then, the sample was dried at 473 K for 10 h. The syntheses of different (5 and 15 wt.%) loading of triflic acid on Zr-TMS were carried out by varying the wt.% ratios of

Zr-TMS and $\text{CF}_3\text{SO}_3\text{H}$. Triflic acid functionalized Zr-TMS are designated as f-Zr-TMS-5, -15 and -30.

2.3. Catalyst characterization

The synthesized materials were mainly characterized by powder X-ray diffraction (XRD) for phase purity and crystallinity, N_2 adsorption–desorption techniques for specific surface area, total pore volume and average pore diameter, Fourier transform infrared (FTIR) spectroscopy for functional group confirmation, elemental analysis for C and S to measure the triflic acid loading in the material, temperature-programmed desorption (TPD) of NH_3 for total acidity, scanning electron microscopy (SEM) for the particle size and morphology, transmission electron microscopy (TEM) to view the crystalline structure and thermogravimetric-differential thermal analysis (TG-DTA and DTG) to study the decomposition and thermal stability of the catalysts.

The powder X-ray diffraction patterns of synthesized Zr-TMS and f-Zr-TMS were recorded on a Rigaku D MAX III VC (Ni-filtered Cu $\text{K}\alpha$ radiation, $\lambda = 1.5404 \text{ \AA}$). The BET surface area, total pore volume, and average pore diameter were measured by N_2 adsorption–desorption method by NOVA 1200 (Quantachrome) at 77 K. The FTIR spectra were obtained in a range of $400\text{--}4000 \text{ cm}^{-1}$ on a Shimadzu FTIR 8201 PC using a Diffuse Reflectance scanning disc technique. Elemental analysis for C and S were done by EA1108 elemental analyzer (Carlo Erba Instruments). Temperature-programmed desorption measurements were carried out to measure the acid strength of f-Zr-TMS with various loading of triflic acid, and Zr-TMS using ammonia as an adsorbate [32–34]. The SEM micrographs of Zr-TMS and f-Zr-TMS materials were taken by Jeol-JSM-5200 scanning microscopy. TEM was performed on a Jeol JEM-1200EX instrument with 100 kV of acceleration voltage to probe the mesoporosity of the materials. The TG-DTA and DTG analysis of the Zr-TMS and f-Zr-TMS catalysts were carried out with Mettler Toledo 851^e equipment using an alumina pan under a nitrogen (80 ml/min) atmosphere from ambient to 1273 K with the increasing rate of 293 K/min.

2.4. Benzoylation of toluene

High purity dry toluene, A.R. grade *p*-T-Cl and nitrobenzene were used without further purification. The catalyst was activated at 383 K for at least 2 h before use in the experiments, so as to maintain the dry conditions. The liquid phase catalytic benzoylation was performed in a 50 ml round bottom flask fitted with a condenser, N_2 gas supply tube and a septum. The temperature of the reaction vessel was maintained using an oil bath. In a typical run, a mixture of toluene (0.01 mol), *p*-T-Cl (0.01 mol), nitrobenzene (10 ml) and activated catalyst (0.5 gm), was magnetically stirred and heated to attain the reaction temperature

(403 K) in the presence of N_2 gas. The product samples were withdrawn at regular intervals of time and analyzed periodically on a gas-chromatograph (HP 6890) equipped with a flame ionization detector and a capillary column (5 μm thick cross-linked methyl silicone gum, 0.2 mm \times 50 m long). The product samples were also identified by injecting authentic samples and GC–MS (Shimadzu 2000 A) analysis.

Conversion of *p*-T-Cl is defined as the weight percentage of *p*-T-Cl consumed. The turnover rates for *p*-T-Cl conversion (TOF, $10^{-1} \text{ h}^{-1} \text{ mol}^{-1} \text{ S}$) was calculated as the moles of *p*-T-Cl converted per hour over per mol of sulphur. The selectivity to a product is expressed as the amount of a particular product divided by the amount of total products and multiplied by 100.

3. Results and discussion

3.1. Catalyst characterization

The various catalysts used in this study and their physico-chemical properties are presented in Table 1, which lists the elemental analysis highlighting the output of carbon and sulphur (wt.%), loading of $\text{CF}_3\text{SO}_3\text{H}$ (wt.%), BET surface area, and crystal size. These data reveal that f-Zr-TMS catalysts are highly mesoporous. Table 1 also illustrates the amount of NH_3 desorbed from catalysts in different temperature steps, which shows the acidic nature of the catalyst. The detailed characterizations of the catalyst have been reported in our previous reports [30,31].

3.2. Catalytic activity of various catalysts

The results of the catalytic activities in the benzoylation of toluene with *p*-T-Cl using conventional catalyst $\text{CF}_3\text{SO}_3\text{H}$, Zr-TMS and various amounts of $\text{CF}_3\text{SO}_3\text{H}$ anchored over Zr-TMS (f-Zr-TMS) are depicted in Table 2. The main product of the reaction is 4,4'-DMBP. A small amount of 2,4'-DMBP is also observed. The formation of 4,4'-DMBP and 2,4'-DMBP results from the aromatic substitution of toluene. The activities of various catalysts are compared under identical reaction conditions using data after 8 h run.

The conversion of *p*-T-Cl, rate of *p*-T-Cl conversion, product distribution and 4,4'-DMBP to 2,4'-DMBP ratio depend on the type of catalysts used. As can be seen from the Table 2, f-Zr-TMS-30 catalyst is found to be more active than any other catalysts. Zr-TMS is less active due to its lower acidic nature. The conversion of *p*-T-Cl (wt.%), rate of *p*-T-Cl conversion ($10^{-1} \text{ h}^{-1} \text{ mol}^{-1} \text{ S}$) and selectivity (wt.%) for 4,4'-DMBP over f-Zr-TMS-5, f-Zr-TMS-15, f-Zr-TMS-30 and Zr-TMS after 8 h of reaction time are found to be 46.0, 50.7, 54.0, 22.4 (wt.%), 13.2, 14.5, 15.5, 6.4 ($10^{-1} \text{ h}^{-1} \text{ mol}^{-1} \text{ S}$) and 75.9, 73.5, 74.2, 78 (wt.%), respectively. $\text{CF}_3\text{SO}_3\text{H}$ produces 20.1 wt.% 2,4'-DMBP and 76.4 wt.% 4,4'-DMBP at 87.5 wt.% conversion level of

Table 1
Physico-chemical properties of catalysts

Catalyst	Elemental analysis (output) (wt.%)		Loading of CF ₃ SO ₃ H (wt.%)		BET ^a surface area (m ² g ⁻¹)	Crystal ^b size (μm)	NH ₃ desorbed (mmol g ⁻¹)					NH ₃ chemisorbed at 303 K (mmol g ⁻¹) ^c
	C	S	Input	Output			303–343 K	343–383 K	383–423 K	423–473 K	473–573 K	
Zr-TMS	–	–	–	–	371	0.33	0.07	0.13	0.16	0.10	0.04	0.50
f-Zr-TMS-5 ^d	0.98	1.01	5.0	4.7	355	0.37	0.12	0.20	0.26	0.13	0.06	0.77
f-Zr-TMS-15 ^d	1.33	2.79	15.0	13.0	320	0.38	0.18	0.30	0.35	0.16	0.06	1.05
f-Zr-TMS-30 ^d	2.00	4.86	30.0	22.8	284	0.40	0.18	0.44	0.63	0.25	0.05	1.55

^a Measured by N₂ adsorption–desorption at 77 K.

^b Measured by Jeol SEM (JSM-5200).

^c Total acid sites determined in the solid catalyst by NH₃ adsorption–desorption.

^d Numbers denote wt.% (input) of triflic acid loading over Zr-TMS.

Table 2
Benzoylation of toluene^a

Catalyst	Reaction time (h)	<i>p</i> -T-Cl ^b conversion (wt.%)	TOF ^c (10 ⁻¹ h ⁻¹ mol ⁻¹ S)	Product distribution ^d (wt.%)			4,4'-DMBP/2,4'-DMBP ^e
				2,4'-DMBP	4,4'-DMBP	Others	
Zr-TMS	8	22.4	6.4	22	78	0	3.5
	24	42.2	4.0	15.5	78.6	5.9	5.0
f-Zr-TMS-5	8	46.0	13.2	22.1	75.9	2.0	3.4
	24	72.0	6.8	23.0	73.3	3.7	3.1
f-Zr-TMS-15	8	50.7	14.5	22.5	73.5	4.0	3.2
	24	82.1	7.8	21.4	74.1	4.5	3.4
f-Zr-TMS-30	8	54.0	15.5	22.5	74.2	3.3	3.2
	24	85.0	8.1	22.8	73.9	3.3	3.2
CF ₃ SO ₃ H	0.25	87.5	420.1	20.1	76.4	3.5	3.8
	3	100	40.0	21.2	75.2	3.6	3.5

^a Reaction conditions: catalyst (g) = 0.5; toluene (mol) = 0.01; *p*-toluoyl chloride (mol) = 0.01; reaction temperature (K) = 403; nitrobenzene (ml) = 10.

^b *p*-T-Cl: *para*-toluoyl chloride.

^c TOF = moles of *p*-T-Cl transformed per second per mol of sulphur.

^d 2,4'-DMBP: 2,4'-dimethylbenzophenone; 4,4'-DMBP: 4,4'-dimethylbenzophenone.

^e Ratio of 4,4'-dimethylbenzophenone/2,4'-dimethylbenzophenone.

p-T-Cl after 0.25 h reaction time. Amongst the f-Zr-TMS with various loadings of triflic acid studied, f-Zr-TMS-30 revealed the highest *p*-T-Cl conversion and rate of *p*-T-Cl conversion, which may be attributed to its stronger acid sites as seen from NH₃ desorption experiment (Table 1). In order to gain an understanding of the acidity of the catalyst, the desorption of NH₃ was carried out in five steps (303–343, 343–383, 383–423, 423–473 and 473–573 K) after allowing the catalyst to adsorb ammonia at room temperature and flushed with nitrogen to remove physisorbed ammonia. Table 1 also shows the total number of acid sites (determined via NH₃ chemisorbed at 303 K) of Zr-TMS, f-Zr-TMS with various loadings of triflic acid. The quantita-

tive distributions of the acid sites (in the five regions) are also shown.

The total number of acid sites on the catalysts was found to increase proportionally with increased loading of triflic acid over Zr-TMS. The total number of acid sites on the Zr-TMS was found to be 0.50 mmol g⁻¹. The total amount of NH₃ chemisorbed at 303 K was 0.77 mmol g⁻¹ for f-Zr-TMS-5, 1.05 mmol g⁻¹ for f-Zr-TMS-15 and 1.55 mmol g⁻¹ for f-Zr-TMS-30. Triflic acid alone is also known to be a superacid [35]. The catalysts used in this study, show the following decreasing order of activity after 8 h of reaction time: CF₃SO₃H > f-Zr-TMS-30 > f-Zr-TMS-15 > f-Zr-TMS-5 > Zr-TMS. The results indicate

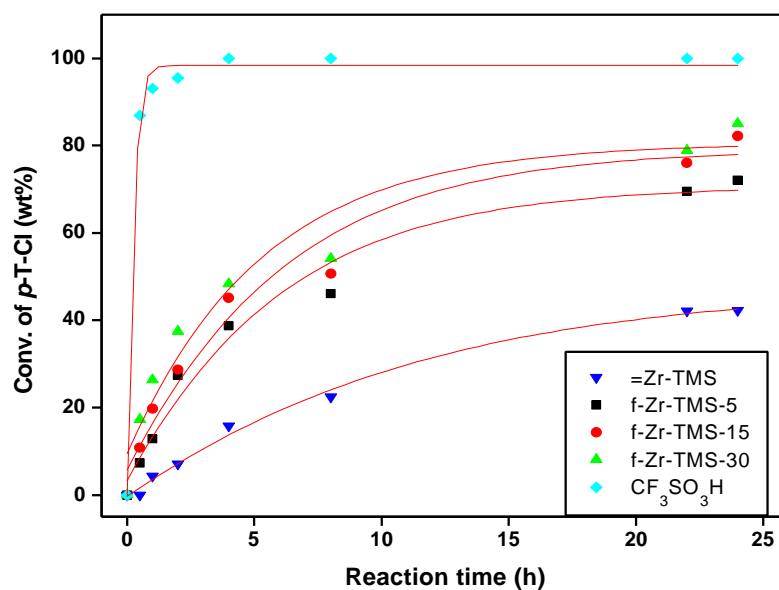


Fig. 1. Conversion of *p*-T-Cl (wt.%) vs. reaction time over various catalysts. Reaction conditions as in footnote 'a' of Table 2.

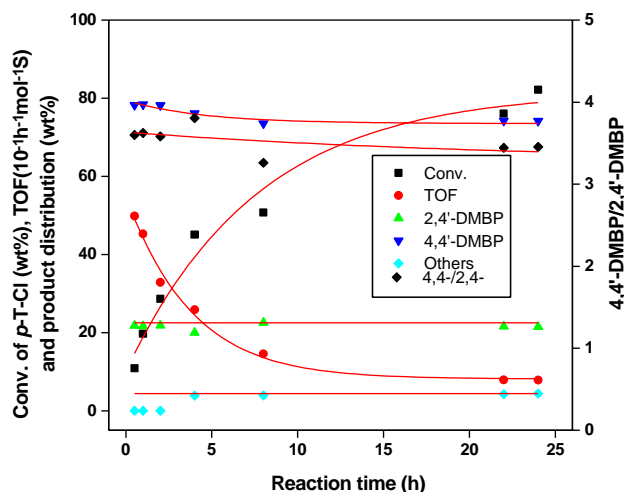


Fig. 2. Effect of reaction time on the conversion of *p*-T-Cl (wt.%), TOF ($10^{-1} \text{ h}^{-1} \text{ mol}^{-1} \text{ S}$), product distribution (wt.%) and 4,4'-DMBP/2,4'-DMBP isomer ratio using f-Zr-TMS-15. Reaction conditions as in footnote 'a' of Table 2.

that mainly *ortho*- and *para*-substitutions take place over f-Zr-TMS catalyst, which is expected for an electrophilic aromatic substitution pathway [20].

3.3. Duration of the run

The conversion of *p*-T-Cl as a function of reaction time for the benzylation of toluene over various f-Zr-TMS (5, 15 and 30 wt.% TFA) and other catalysts such as Zr-TMS and TFA are given in Fig. 1. Increasing reaction time increased the conversion of *p*-T-Cl over all catalysts. f-Zr-TMS-30 showed considerably superior performance throughout the reaction and its activity is found to be higher compared with those of other catalysts. The reason could be, the higher strength and number of acid sites. Zr-TMS is found to be much less active. $\text{CF}_3\text{SO}_3\text{H}$ is the most active catalyst and within 0.25 h, 87.5 wt.% conversion of *p*-T-Cl is obtained (Fig. 1). The catalytic activity of various catalysts used in this study after 24 h of reaction time can be arranged in the following order: $\text{CF}_3\text{SO}_3\text{H} > \text{f-Zr-TMS-30} > \text{f-Zr-TMS-15} > \text{f-Zr-TMS-5} > \text{Zr-TMS}$.

3.4. Influence of reaction time using f-Zr-TMS-15

The influence of reaction time on the conversion of *p*-T-Cl, product distribution and 4,4'-DMBP/2,4'-DMBP using f-Zr-TMS-15 as catalyst at 403 K is presented in Fig. 2. The conversion of *p*-T-Cl increased almost linearly up to 22 h of reaction time and then a marginal increase in the conversion of *p*-T-Cl is observed. *p*-T-Cl along with toluene leads mainly to 4,4'-DMBP with 78 wt.% selectivity within 0.5 h reaction time and decreases to 74.1 wt.% after 24 h. The results show that the reaction time influenced the conversion of *p*-T-Cl, but did not affect significantly the 4,4'-DMBP/2,4'-DMBP isomer ratio to a great extent.

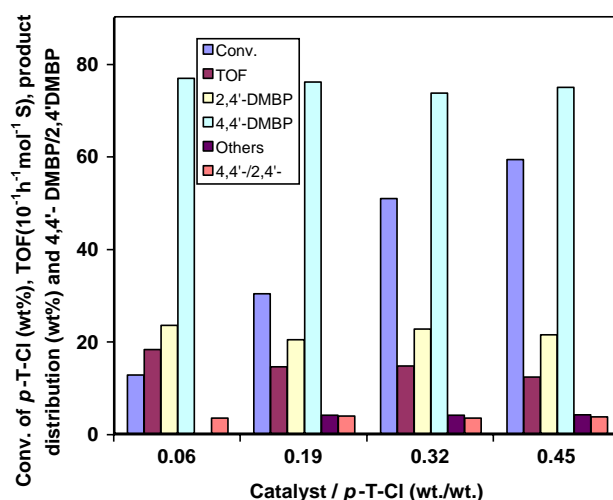


Fig. 3. Effect of catalyst/*p*-T-Cl (w/w) ratio on the conversion of *p*-T-Cl (wt.%), TOF ($10^{-1} \text{ h}^{-1} \text{ mol}^{-1} \text{ S}$), product distribution (wt.%) and 4,4'-DMBP/2,4'-DMBP isomer ratio. Other reaction conditions as in footnote 'a' of Table 2.

3.5. Influence of catalyst / *p*-T-Cl (w/w) ratio

To study the effects of catalyst concentration on the conversion of *p*-T-Cl, rate of *p*-T-Cl conversion, product distribution and 4,4'-/2,4'-isomer ratio, the catalyst concentration (catalyst/*p*-T-Cl ratio (w/w)) was increased from 0.06 to 0.45 and the results are depicted in Fig. 3. The different ratios of catalyst/*p*-T-Cl were obtained by varying the amount of catalyst and keeping the concentration of *p*-T-Cl constant. The conversion of *p*-T-Cl increased from 12.6 to 59.1 wt.% as the catalyst concentration increases from 0.06 to 0.45. No change in the product distribution is seen against the change in catalyst concentration. The rate

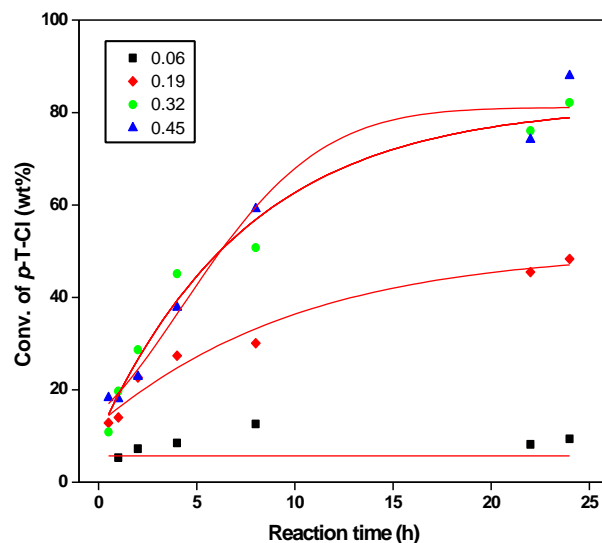


Fig. 4. Effect of different catalyst/*p*-T-Cl (w/w) ratio on the conversion of *p*-T-Cl (wt.%) vs. reaction time (h). Other reaction conditions as in footnote 'a' of Table 2.

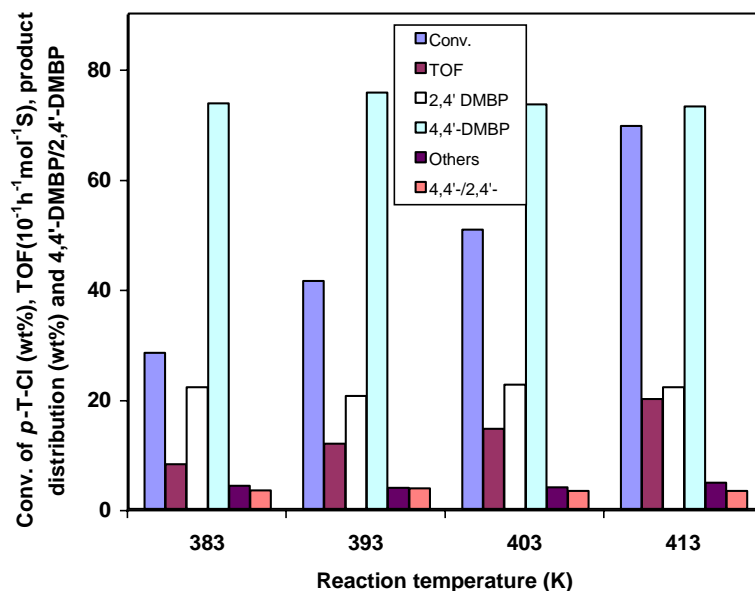


Fig. 5. Effect of different reaction temperatures on the conversion of *p*-T-Cl (wt%), TOF ($10^{-1} \text{ h}^{-1} \text{ mol}^{-1} \text{ S}$), product distribution (wt%) and 4,4'-DMBP/2,4'-DMBP isomer ratio. Other reaction conditions as in footnote 'a' of Table 2.

of *p*-T-Cl conversion (TOF) decreases continuously due to the increase in catalyst concentration and a corresponding increase in the concentration of sulphur in the total amount of catalyst used in the benzoylation of toluene.

Fig. 4 shows the conversion profile of *p*-T-Cl versus reaction time using different catalyst concentrations (catalyst/*p*-T-Cl (w/w) ratio). It may be seen that the catalyst/*p*-T-Cl (w/w) ratio had a strong effect on the conversion of *p*-T-Cl. A rapid increase in the conversion of *p*-T-Cl is observed at the early stages (up to 8 h) of the reaction over all catalyst/*p*-T-Cl (w/w) ratios. The maximum

increase in the conversion of *p*-T-Cl with reaction time is found for a catalyst/*p*-T-Cl (w/w) ratio of 0.45.

3.6. Influence of reaction temperature

The effect of reaction temperature was studied on the rate of benzoylation of toluene with *p*-toluoyl chloride as benzoylating agent over f-Zr-TMS-15 catalyst in the temperature range 383–413 K using a toluene/*p*-T-Cl molar ratio as 1. When the temperature is increased from 383 to 413 K, both the conversion of *p*-T-Cl and TOF increased from 28.3

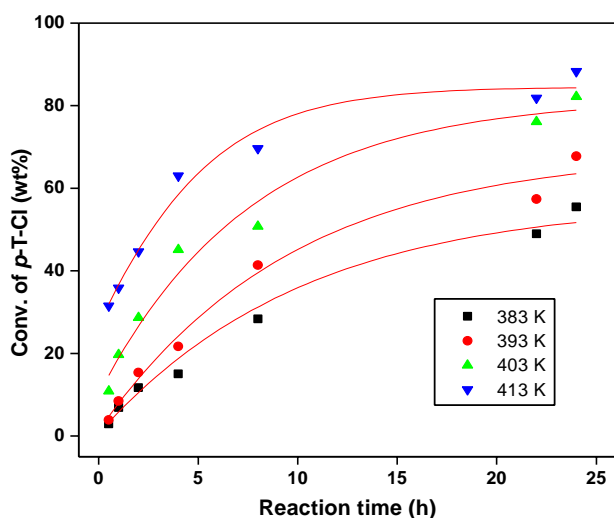


Fig. 6. Effect of reaction temperature (K) on the conversion of *p*-T-Cl (wt%) over f-Zr-TMS catalyst with reaction time (h). Other reaction conditions as in footnote 'a' of Table 2.

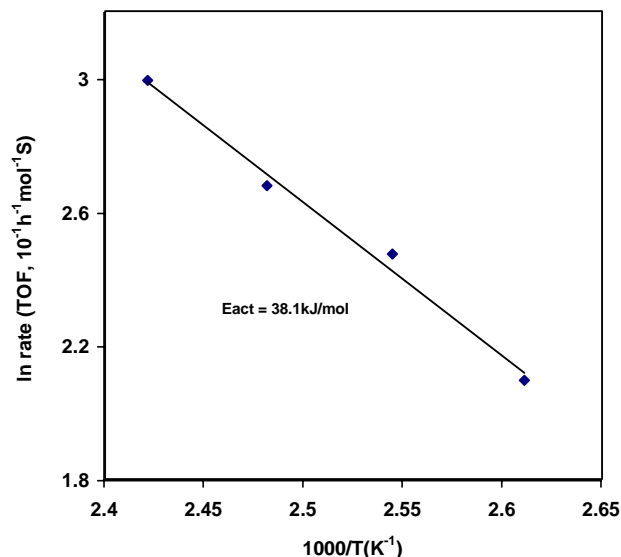


Fig. 7. Arrhenius plot for the benzoylation of toluene by *p*-T-Cl over f-Zr-TMS-15.

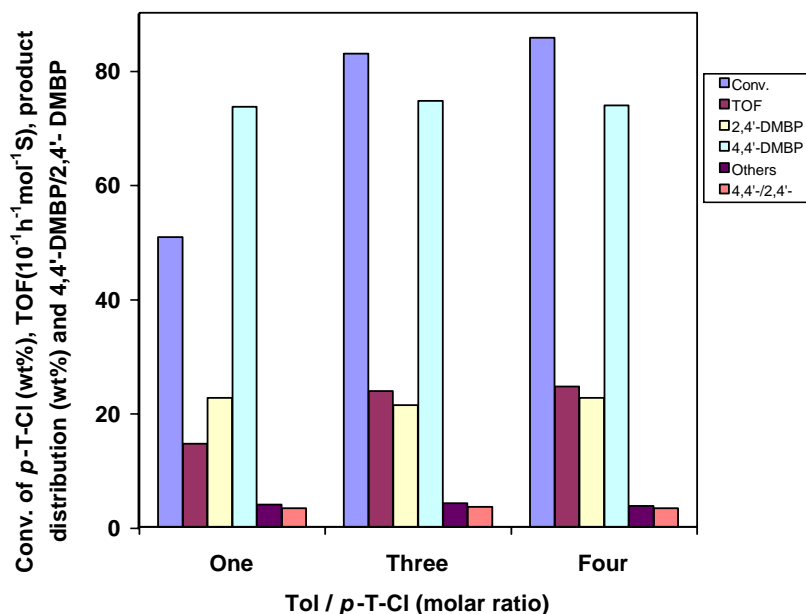


Fig. 8. Effect of Tol/*p*-T-Cl molar ratio on the conversion of *p*-T-Cl (wt%), TOF ($10^{-1} \text{ h}^{-1} \text{ mol}^{-1} \text{ S}$), product distribution (wt%) and 4,4'-DMBP/2,4'-DMBP isomer ratio. Other reaction conditions as in footnote 'a' of Table 2.

to 69.5 wt.% and from 8.1 to 19.9 ($10^{-1} \text{ h}^{-1} \text{ mol}^{-1} \text{ S}$), respectively. However, the selectivity for 4,4'-DMBP remains nearly unchanged with the increase in reaction temperature, as shown in Fig. 5.

One of the reasons for the increased rates at higher temperature may be ascribed to an enhancement of the rate of diffusion of *p*-T-Cl inside the channel of the catalyst, however, reaction rates are usually more temperature dependant than rate of diffusion [36]. Increasing the reaction temperature increases the catalytic activity and the conversion of *p*-T-Cl increases sharply at the initial stages (8 h) of the reaction and finally (22 h) reaches a relatively steady state value over all temperatures as shown in Fig. 6.

The apparent activation energy of *p*-T-Cl conversion over f-Zr-TMS-15 catalyst is estimated to be 38.11 kJ/mol as it is depicted in Fig. 7 in the temperature range of 383–413 K.

3.7. Influence of molar ratios of the reactants

The results of the influence of Tol/*p*-T-Cl molar ratios on the *p*-toluoyl chloride conversion, TOF, product distribution and 4,4'-DMBP/2,4'-DMBP ratio is shown in Fig. 8.

The ratios were changed by keeping the amount of *p*-T-Cl as constant. The data at 403 K show that, when Tol/*p*-T-Cl ratio is increased from 1 to 4, the conversion

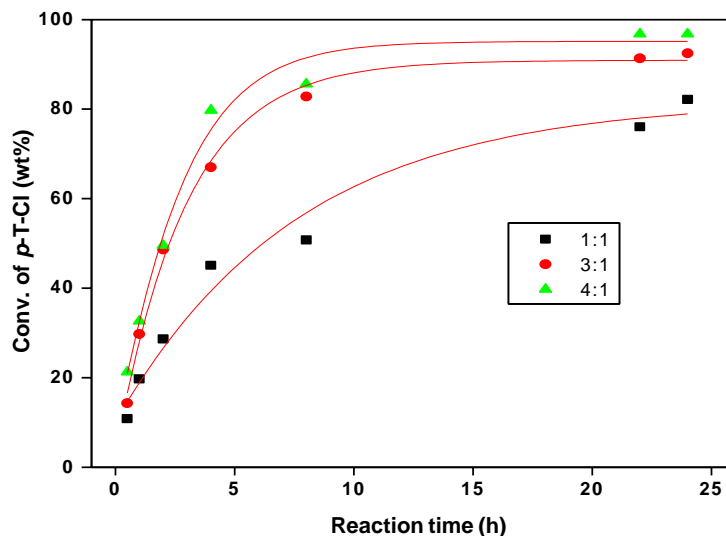


Fig. 9. Effect of different molar ratios of Tol/*p*-T-Cl molar ratio on the conversion of *p*-T-Cl (wt%) vs. reaction time (h). Other reaction conditions as in footnote 'a' of Table 2.

Table 3
Recycling of f-Zr-TMS-15 in benzylation reaction^a

Cycle	Loading of CF ₃ SO ₃ H (wt.%)	Conversion of <i>p</i> -T-Cl ^b (wt.%)	Product distribution ^c (wt.%)			4,4'-DMBP/2,4'-DMBP ^d	TOF ^b (10 ⁻¹ h ⁻¹ mol ⁻¹ S)	Crystallinity (%) ^e
			2,4'-DMBP	4,4'-DMBP	Others			
Fresh	15.0	50.7	22.5	73.5	4.0	3.2	14.5	100
1st recycle	14.1	49.2	21.6	74.5	3.9	3.4	14.9	98

^a Reaction conditions: catalyst (g) = 0.5; toluene (mol) = 0.01; *p*-toluoyl chloride (mol) = 0.01; reaction temperature (K) = 403; nitrobenzene (ml) = 10.

^b *p*-T-Cl: *para*-toluoyl chloride.

^c TOF = moles of *p*-T-Cl transformed per second per mol of sulphur.

^d 2,4'-DMBP: 2,4'-dimethylbenzophenone; 4,4'-DMBP: 4,4'-dimethylbenzophenone.

^e By X-ray diffraction.

of *p*-T-Cl and rate of *p*-T-Cl conversion increase linearly from 50.7 wt.% and 14.5 (10⁻¹ h⁻¹ mol⁻¹ S) to 85.6 wt.% and 24.5 (10⁻¹ h⁻¹ mol⁻¹ S), respectively. In addition, the selectivity to 4,4'-DMBP is found to be unaffected over the wide range of Tol/*p*-T-Cl ratio. The conversion of *p*-T-Cl vs. reaction time increases with all molar ratios of Tol/*p*-T-Cl. A higher increase in the *p*-T-Cl conversion with reaction time is observed when Tol/*p*-T-Cl molar ratio of four is used in the benzylation of toluene (Fig. 9).

3.8. Catalyst recycling

In order to check the stability and catalytic activity, the catalyst was recycled (fresh + one cycle) by using f-Zr-TMS-15 in the benzylation of toluene. The results are presented in Table 3. After workup of the reaction mixture, the catalyst was separated by filtration, washed with acetone and activated for 16 h at 473 K in the presence of air before use in the next experiment. Thus, the recovered catalyst after each reaction was characterized for its chemical composition by elemental analysis and crystallinity by X-ray diffraction. Elemental analysis showed a downward trend in the content of anchored CF₃SO₃H of f-Zr-TMS-15 catalyst after one cycle. A slight decline was observed in the *p*-T-Cl conversion from 50.7 to 49.2 wt.%, when the catalyst was reused for first time. The leaching of the CF₃SO₃H from the Zr-TMS catalysts by HCl (formed during the reaction) may be attributed for the decrease in catalytic activity after one cycle. The result reported here are in good agreement with the earlier reported data for the acylation of biphenyl using f-Zr-TMS catalysts [30,31].

4. Conclusions

In summary, benzylation of toluene to 4,4'-DMBP reactions were performed on f-Zr-TMS-5, f-Zr-TMS-15, f-Zr-TMS-30, Zr-TMS and TFA catalysts. f-Zr-TMS-30 catalyst catalyzes the benzylation of toluene efficiently with *para*-toluoyl chloride and is superior to other f-Zr-TMS catalysts due to its higher acidity. The conventional homogeneous catalyst, CF₃SO₃H, shows higher activity. Total acidity obtained at 303 K of Zr-TMS and f-Zr-TMS

with different wt.% loading of triflic acid show direct co-relationship between acidity and catalytic activity in the benzylation of toluene. The influence of the duration of the run, catalyst concentration, reaction temperature and Tol/*p*-T-Cl molar ratio on the catalyst performance is examined in order to optimize the conversion of *p*-T-Cl and selectivity to 4,4'-DMBP. The conversion of *p*-T-Cl using f-Zr-TMS-15 increased significantly with an increase in reaction time, catalyst concentration, reaction temperature and Tol to *p*-T-Cl molar ratio. f-Zr-TMS-15 was recycled one time and a decrease in *p*-T-Cl conversion is observed after one cycle, which is related to a minor leaching of CF₃SO₃H from the catalyst. The formation of acylated products of toluene is explained by an electrophilic attack of acyl cation (R-CO⁺; where R = CH₃-C₆H₅) on the toluene ring, whose formation is facilitated by acid sites on f-Zr-TMS catalysts.

References

- [1] U. Beck, in: W. Gerhartz, Y.Y. Stephen, F.T. Campbell, R. Pfelekom, J.F. Rounsaville (Eds.), Ullmann's Encyclopedia of Industrial Chemistry, vol. A15, VCH, Weinheim, 1986, p. 91.
- [2] M. Nakatsuka, Y. Tanabe, K. Yoshikawa, JP 08,290,668 (1996).
- [3] M. Windholz (Ed.), Merck Index, An Encyclopedia of Chemical Drugs and Biochemicals, 10th ed., Merck and Co. Inc., Rahway, NJ, 1983, p. 7199.
- [4] K. Beyer, W. Bergfeld, W.O. Berndt, R. Boutwell, W. Carlton, D. Hoffmann, A.L. Schroeter, Final Report of the Cosmetic Ingredient Review, 1982–1983, p. 25.
- [5] H. Limpricht, Annalen 91 (1900) 312.
- [6] A.L. Klebanski, K.K. Tehevychatova, Zh. Obshch. Khim. 5, 535 (1935), C.A. 29,6879 (1935).
- [7] R.E. Wilson, E.W. Fuller, J. Ind. Eng. Chem. 14 (1922) 406.
- [8] H.A. Fahim, J. Chem. Soc. 520 (1949).
- [9] R.C. Fusan, G.R. Barker, B. Vittinberga, J. Am. Chem. Soc. 81 (1959) 4858.
- [10] H. Stefan, W.F. Short, J. Chem. Soc. 117 (1920) 510.
- [11] S. Kahn, N.J. Rutherford, US Patent 3,642,906 (1972).
- [12] M. Walker, US Patent 6,362,375 (2002).
- [13] T. Yamaguchi, Appl. Catal. 61 (1990) 1.
- [14] H.C. Brown, G. Marino, J. Am. Chem. Soc. 81 (1959) 3308.
- [15] G.A. Olah, Friedel-Crafts and Related Reactions, vol. 1–4, Wiley-Interscience, New York, London, 1963–1964.
- [16] G.A. Olah, Friedel-Crafts Chemistry, Wiley-Interscience, New York, London, Sydney, Toronto, 1973.

- [17] G.A. Olah, G.K.S. Prakash, J. Sommer, *Superacids*, Wiley–Interscience, New York, Brisbane, Toronto, 1985.
- [18] C. Venkatesan, T. Jaimol, P. Moreau, A. Finiels, A.V. Ramaswamy, A.P. Singh, *Catal. Lett.* 75 (1/2) (2001) 119.
- [19] P. Ratnasamy, A.P. Singh, S. Sharma, *Appl. Catal. A.* 135 (1996) 25.
- [20] G.A. Olah, R. Malhotra, S.C. Narang, J.A. Olah, *Synthesis* (1978) 672.
- [21] P. Laszlo, M.T. Montaufer, *Tetrahedron Lett.* 32 (1991) 1561.
- [22] K. Tanabe, T. Yamaguchi, K. Akiyama, A. Mitoh, K. Iwabuchi, K. Isogai, in: *Proceedings of the 8th International Congress on Catalysis*, Berlin, Verlag Chemie, Berlin, 1984, p. 601.
- [23] K. Arata, M. Hino, *Appl. Catal.* 59 (1990) 197.
- [24] K. Arata, K. Yabe, I. Toyoshima, *J. Catal.* 44 (1976) 385.
- [25] K. Arata, H. Nakamura, M. Shouji, *Appl. Catal. A.* 197 (2000) 213.
- [26] V.I. Parvulescu, H. Bonnemann, V. Parvulescu, B. Endruschat, A.Ch.W. Rufinska, B. Tesche, G. Poncelet, *Appl. Catal. A.* 214 (2001) 273.
- [27] J.W. Brockington, R.H. Bennett, US Patent 3,970,721 (1976).
- [28] J.F. Joly, C. Marcilly, E. Benazzi, US Patent 5,336,833 (1994).
- [29] S.I. Hommeltoft, Eur. Patent 0,987,237A, (2000).
- [30] M. Chidambaram, C. Venkatesan, P.R. Rajamohanam, A.P. Singh, *Appl. Catal. A.* 244 (2003) 27.
- [31] M. Chidambaram, D. Curulla-Ferre, A.P. Singh, B.G. Anderson, *J. Catal.* 220 (2003) 442.
- [32] N.C. Marziano, L.D. Ronchin, C. Tortato, A. Zingales, A.A. Sheikh-Osman, *J. Mol. Catal. A.* 174 (2001) 265.
- [33] M. Chamumi, D. Brunel, F. Fajula, P. Geneste, P. Moreau, J. Solof, *Zeolites* 14 (1994) 283.
- [34] A. Corma, M.I. Fornes, J.M. Juan-Rajadell, L. Neito, *Appl. Catal. A.* 116 (1994) 151.
- [35] R.D. Howells, J.D. McCown, *Chem. Rev.* 77 (1977) 69.
- [36] J.S. Reddy, S. Sivasanker, P. Ratnasamy, *Zeolites* 12 (1992) 135.