

Friedel–Crafts benzylation of diphenyl oxide over zirconia supported 12-tungstophosphoric acid

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Abstract

Liquid phase benzylation of diphenyl oxide (DPO) to 4-(benzoyl)-diphenyl oxide (*p*-isomer) with benzoyl chloride (BC) has been investigated with 12-tungstophosphoric acid supported on zirconia (TPA/ZrO₂) as the catalyst. Among the catalysts, 15 wt.% TPA/ZrO₂ calcined at 750 °C is found to be more active than others in the benzylation reaction. The acid strengths of different TPA loaded catalysts are estimated by TPD of NH₃ and among these 15 wt.% TPA/ZrO₂ calcined at 750 °C has the highest acidity and hence more active in the reaction. The optimization of reaction conditions of benzylation of DPO by BC is performed with 15 wt.% TPA/ZrO₂ calcined at 750 °C (higher acidity) by varying catalyst concentration, 1–5 (wt.% of reaction mixture), temperature, 100–140 °C and DPO:BC molar ratio 1–15. Under the optimized reaction conditions, conversion of benzoyl chloride (39.3%) gave high selectivity to 4-(benzoyl) diphenyl oxide (97.4%) and remaining 2-(benzoyl) diphenyl oxide in 3 h. The reaction is found to be heterogeneously catalyzed and no contribution from homogeneous (leached) TPA into reaction medium.

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1. Introduction

Friedel–Crafts alkylation and acylation of aromatic hydrocarbons have been studied extensively using Lewis acid catalysts, such as, BF₃, AlCl₃, FeCl₃, TiCl₄ and protonic acid like HF, H₂SO₄ [1–3]. But, the use of conventional Lewis and mineral acid catalysts has lead to environmental problems, especially in large-scale production sites. Hence, there is a need to find newer catalyst systems to replace conventional for the Friedel–Crafts reactions. During the last three decades, efforts have been made to replace conventional catalysts with solid acid catalyst systems for Friedel–Crafts reactions. Among the solid acids reported, sulfated zirconia have been found to be highly active catalysts in many acid catalyzed reactions [4,5]. However, these catalysts suffer from the drawbacks, like poor thermal stability and tendency to form volatile sulfur compounds during catalysis, regeneration by oxidation and leaching with water forming reactions,

limit their applications in industry [6]. Similarly, zeolite H-beta and acid treated clays have been reported as replacement to the conventional Lewis acid catalysts for alkylation reactions and these also have limitations for known reasons in the literature. In recent years alternate to existing solid acid catalysts, development of metal oxide supported catalysts, such as, zirconia supported heteropoly acid catalysts have gain importance, since these provide advantages over others like higher thermal stability, cost effective and eco-friendly systems for applications in large-scale productions. Hence, our research group at NCL, Pune is involved in the development of new metal oxides supported heteropoly acid catalysts for alkylation and acylation of aromatic substrates and have published our work on the above topic [7,8].

Acylation of an aromatic substrates has been carried out using solid acid catalysts such as sulfated zirconia [9,10], heteropoly acids [11,12] and acid activated clays [9–12]. Friedel–Crafts acylation of aromatic compounds is pioneered by Izumi et al. [13]. Silica supported TPA catalyst was used for the acylation of *p*-xylene with benzoyl chloride and anisole with acetic anhydride [14] and have reported that TPA was unchanged on silica surface after the reaction.

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Recently, TPA supported over hexagonal mesoporous silica was used as a solid acid catalyst in the synthesis of aceto-veratrone via acylation of veratrol by acetic anhydride [15]. Alkylation of DPO with long chain olefins using smectite clay [16] and benzylation with benzyl chloride using sulfated zirconia as a catalyst [17] have been reported. Alkylation of DPO with olefins, alcohols and benzoyl chloride give commercially important alkylated products, for instance, heat transfer fluids and perfumery compounds. In view of the importance of the reaction products, we report in this paper our data on the catalytic performance of TPA/ZrO₂ catalyst in benzylation of DPO using BC to give selectively monoalkylated product.

2. Experimental

2.1. Materials

12-Tungstophosphoric acid and benzoyl chloride were purchased from s.d. fine chemicals Ltd., Mumbai. Zirconium oxychloride and diphenyl ether were obtained from Loba Chemie Ltd., Mumbai. Methanol (AR grade) was purchased from E-Merck India Ltd., Mumbai. All the above materials were used as-received in the catalyst preparation and benzylation experiments. Zeolites H-beta, H-ZSM-5 and H-Y recovered by calcining NH₄-Y were obtained from Catalysis Pilot Plant (CPP-NCL, Pune). H-Mordenite was obtained from PQ Zeolites BV, Netherlands. All catalysts used in the reactions were in the powder form and were activated prior to their use in the reaction.

2.2. Preparation of TPA/ZrO₂ catalysts

Zirconia supported heteropoly acid catalysts were prepared by impregnating TPA on zirconium hydroxide obtained by the hydrolysis of zirconium oxychloride following the procedure described in our earlier publication [7]. Dried catalysts were calcined in air at 750 °C. Catalysts with different TPA loading from 5 to 30 wt.% were prepared and calcined at 750 °C. Similarly, 15 wt.% TPA/SiO₂ was prepared as above using silica gel and calcined at 750 °C. Silica gel support was prepared by known procedure [18].

The surface area of the catalysts was measured by the nitrogen BET method using an area meter. The acidity of TPA/ZrO₂ with different TPA loading measured by TPD of ammonia and data are listed in Table 1. It is seen that acidity

(NH₃ nm⁻²) and surface area increased with TPA loading up to 15 wt.% and then decreased with further increase in loading. Higher acidity of 15 wt.% TPA/ZrO₂ catalyst among different loading is due to monolayer coverage of TPA on zirconia [7].

2.3. Aromatic benzylation

The liquid phase benzylation of DPO by BC was carried out in a 50 ml round bottom flask equipped with heating arrangement to the required reaction temperature (constant temperature-oil bath), water condenser and a magnetic stirrer for agitation. In a typical run, DPO and BC were mixed in required mole ratio and added to the pre-activated catalyst. Excess of DPO are taken in most of the runs and the catalytic activity with respect to the conversion of limiting reagent BC is monitored as a function of time under the pre-decided reaction conditions. The reaction mixture was magnetically stirred and heated to the required temperature at atmospheric pressure. As soon as the catalyst comes in contact with the reaction mixture, the color of the catalyst changed from white to faint brown and with time changed to dark wine red, which indicated the progress of the reaction. Samples of the reaction mixture withdrawn at regular intervals of time were analyzed by a gas chromatograph (Shimadzu 14B GC) equipped with a SE-52 packed column, coupled with FID detector. Authenticity of the products was confirmed by GCMS (Shimadzu QP-5000) and NMR analysis. From the gas chromatographic analysis, percentage conversion of benzoyl chloride and selectivity for products were calculated and used in the interpretation of data of the reaction.

2.4. Characterization techniques

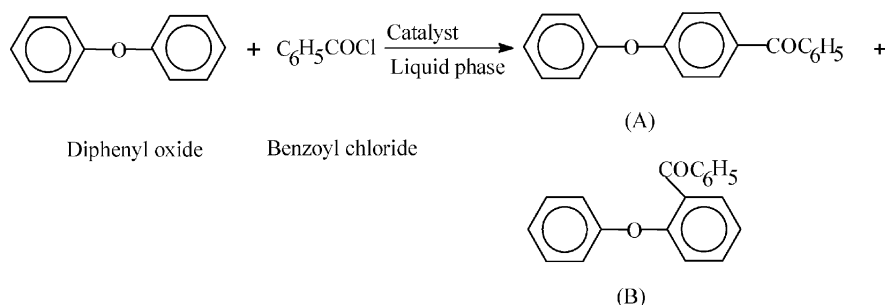
Crystallographic identification of the samples were performed using X-ray powder diffraction with Cu K α radiation (Rigaku model D/MAXIII VC, Japan, $\lambda = 1.5418 \text{ \AA}$). Surface area of heteropoly acid catalysts was measured by nitrogen physisorption on a Quantachrome Nova-1200 surface area analyzer. Acidity and acid strength distribution of catalysts with different TPA loadings were measured by TPD of NH₃. Brönsted and Lewis acidity of catalysts with different TPA loadings were monitored by pyridine adsorption FT-IR spectroscopy (NICOLET MODEL 60XB, 4 cm⁻¹ resolution and averaged over 500 scans) and the data on the above has already been published in our earlier paper [7].

3. Results and discussion

Liquid phase benzylation of diphenyl ether (DPO) with benzoyl chloride (BC) catalyzed by 15 wt.% TPA/ZrO₂ calcined at 750 °C under optimized reaction conditions gave *para*-(benzoyl) DPO (A) and *ortho*-(benzoyl) DPO (B) as shown in the reaction scheme:

Table 1
Characteristics of TPA/ZrO₂ catalysts

TPA (wt.%)	Surface area (m ² g ⁻¹)	Acidity (mmol/g)
5	40.2	0.23
10	46.3	0.36
15	53.2	0.46
20	52.3	0.23
30	44.9	0.16



In the benzoylation of DPO, benzoyl chloride gets protonated in presence of a catalyst and electrophilic substitution of carbocation in *ortho*- or *para*- positions of phenyl ring of DPO results in the formation of benzoylated products. In the above reaction, the substitution of carbocation in *para* position is found to be more facile and hence higher selectivity to *para*-(benzoyl) DPO.

3.1. Catalysts characterization

Nitrogen adsorption measurements show that surface area increases with TPA loading up to 15 wt.% and decreases with further increase in loading. For a fixed TPA loading, surface area is found to decrease with increasing calcination temperature. Zirconia calcined at 750 °C mainly exists in monoclinic form with a small amount of the tetragonal form. The tetragonal form of zirconia increases with TPA loading and is fully tetragonal for the catalyst containing 30 wt.% of TPA. When the loading exceeds 15 wt.%, the formation of tungsten oxide crystallites was also observed. Acidity measurements by TPD of ammonia show that the density of acid sites increases with TPA loading and reaches its maximum for the catalyst containing 15 wt.% TPA. For higher loadings, the acid site density decreases due to the decomposition of TPA into its constituent oxides as indicated by the formation of tungsten oxide crystallites as evident from XRD and phosphorous (V) oxide detected by NMR [7].

3.2. Activities of different catalysts in benzoylation of DPO by BC

The catalytic activities of different catalysts, such as, H-beta, H-Y, H-ZSM-5, H-Mordenite, neat TPA and 15 wt.% TPA/SiO₂-calcined at 750 °C tested for their catalytic activities in the benzoylation of DPO under identical reaction conditions are summarized in Table 2. It is seen from the results that TPA (homogeneous) gave the highest conversion of BC (48.6%), followed by H-beta, 15 wt.% TPA/ZrO₂, H-Y and the rest. It is also observed that 15 wt.% TPA/SiO₂ has the poorest activity in the reaction, because it has no acidity required for acid catalyzed reactions. The absence of acidity in 15 wt.% TPA/SiO₂ calcined at 750 °C confirmed that TPA decomposed on SiO₂ support and lost its acidity. Among the zeolite catalysts, H-beta was found to be more active since it was more strong and medium

acid sites and gave higher conversion of benzoyl chloride followed by H-Y (highest acidity and large pore but weaker acid sites). Similarly, poorest activity of H-ZSM-5 might be explained on the basis of its smaller pore size compared with the larger size of the products. While, H-Mordenite has one-dimensional pore with elliptical channels, 6.5 Å × 7.0 Å also has the low activity. Therefore, we took up 15 wt.% TPA/ZrO₂ calcined at 750 °C (which is our purpose) as the catalyst for further investigations on its catalytic performance in the benzoylation of DPO with benzyl chloride.

3.3. Effect of different TPA loading on ZrO₂ in the benzoylation of DPO by BC

Benzoylation experiments were conducted using different TPA loaded (5–30 wt.%) catalysts and the results are presented in Table 3. It is seen that benzoyl chloride conversion increased with increase in TPA loading up to 15 wt.% and decreased further with increase in loading. Since, 15 wt.% catalyst is more acidic than others (Table 1), it gave highest benzoyl chloride conversion (39.3%) under the optimized reaction conditions. However, it is evident from the results presented in Table 3 that the selectivity for *para* product, *p*-(benzoyl) diphenyl ether is highest and almost the same at all conversions of BC.

In order to check the leaching of the TPA into the reaction mixture in the course of the reaction, reaction was carried out for 2 h under optimized reaction conditions. The reaction was then stopped and catalyst was separated by filtration and then same reaction mixture was stirred further for 1 h. It was found that in the absence of the catalyst, there is no further increase in the conversion of BC, which indicated the absence of leaching of TPA. The above study ensured that the reaction was catalyzed only in presence of a catalyst heterogeneously. In addition to this, leaching of TPA (dissolution of P or W) in the filtrate was tested by inductively coupled plasma-optical emission spectroscopy (ICP-OES). This showed the complete absence of P or W in solution, after reaction and confirmed that benzoylation reaction occurred heterogeneously by surface mechanism.

3.4. Effect of calcination temperature on TPA/ZrO₂ in benzoylation of DPO by BC

Benzoylation of DPO was conducted for studying the effect of different calcinations temperatures on 15 wt.%

Table 2
Comparison of the activities of different catalysts in benzoylation of DPO by BC^a

Catalyst	SiO ₂ /Al ₂ O ₃ (molar ratio) ^b	Surface area (m ² /g) ^c	Acidity (mmol/g) ^d	BC conversion (%)	Product distribution (%) ^e	
					2-BDPO	4-BDPO
Neat TPA*		7	–	48.6	23.0	77.0
15 wt.% TPA/ZrO ₂ calcined at 750 °C	–	53.2	0.46	39.3	2.6	97.4
15 wt.% TPA/SiO ₂ calcined at 750 °C	–	16	Nil	9.8	1.9	98.1
H-beta	30	540	0.94	40.4	3.3	96.7
H-Y	13.5	530	2.25	22.5	11.0	89.0
H-Mordenite	20	490	0.72	8.7	–	100
H-ZSM-5	60	364	0.82	3.5	–	100

^a Conditions: catalyst/benzoyl chloride (wt./wt.) = 0.28, temperature = 393 K, diphenyl oxide/benzoyl chloride (molar ratio) = 7, diphenyl oxide = 0.026 mol, time = 3 h.

^b Measured by atomic absorption.

^c Measured by nitrogen BET method using an area meter.

^d Measured by TPD of ammonia.

^e 2-BDPO: 2-(benzoyl) diphenyl oxide; 4-BDPO: 4-(benzoyl) diphenyl oxide.

* Amount of catalyst is taken as per TPA content.

TPA/ZrO₂ catalysts in their catalytic activities in benzoylation of DPO by BC and the results are presented in Table 3. From the data, it was seen that the conversion of benzoyl chloride increased up to the calcination temperature 750 °C and then on further increase in calcination temperature the conversion of BC decreased. This also supports the fact that 15 wt.% TPA/ZrO₂ calcined at 750 °C has the maximum concentration of acid sites (surface density of 7.2 W nm⁻²), where a TPA monolayer covered over the support. Therefore, catalyst calcined at 750 °C was chosen for further study.

3.5. Effect of reaction temperature in benzoylation of DPO by BC

The benzoylation of DPO was carried out in the range of temperatures 100–140 °C to know the effect of tempera-

ture on the conversion of BC and the product selectivities. The effect of temperature on conversion of BC is shown in Fig. 1 along with the reaction conditions (legend). It is seen from the graph that as the temperature is increased from 100 to 140 °C, conversion of BC increased without appreciable change in the selectivity for products. The highest conversion of BC (39.3%) was at 120 °C in 3 h with *o*- and *p*-selectivities 2.6 and 97.4%, respectively. Hence, 120 °C was selected for further optimization of the reaction conditions in the benzoylation reaction.

3.6. Effect of molar ratio of DPO:BC in the benzoylation of DPO by BC

The influence of DPO:BC molar ratio on the conversion of BC and product distribution are presented in Fig. 2. The DPO/BC mole ratio was changed from 1 to 15, keeping other

Table 3
Catalytic data on benzoylation of DPO by BC^a

Catalyst	BC conversion (%)	Product distribution (%) ^b		4-BDPO/2-BDPO ratio
		2-BDPO	4-BDPO	
Effect of TPA loading (wt.%) on ZrO ₂ calcined at 750 °C				
5 wt.% TPA/ZrO ₂	7.5	1.6	98.4	62.3
10 wt.% TPA/ZrO ₂	17.9	2.1	97.9	47.1
15 wt.% TPA/ZrO ₂	39.3	2.6	97.4	37.3
20 wt.% TPA/ZrO ₂	36.8	2.4	97.6	41.5
30 wt.% TPA/ZrO ₂	21.7	2.3	97.7	44.2
Effect of calcination temperature on 15 wt.% TPA/ZrO ₂				
650 °C	21.8	3.5	96.5	27.6
750 °C	39.3	2.6	97.4	37.3
850 °C	10.0	1.9	98.1	52.2
Catalyst recycling				
Fresh	39.3	2.6	97.4	37.3
First recycle	39.0	3.2	96.8	30.1
Second recycle	37.7	4.3	95.7	22.7

^a Conditions: catalyst/benzoyl chloride (wt./wt.) = 0.28, temperature = 120 °C, diphenyl oxide/benzoyl chloride (molar ratio) = 7, diphenyl oxide = 0.026 mol, time = 3 h.

^b 2-BDPO: 2-(benzoyl) diphenyl oxide; 4-BDPO: 4-(benzoyl) diphenyl oxide.

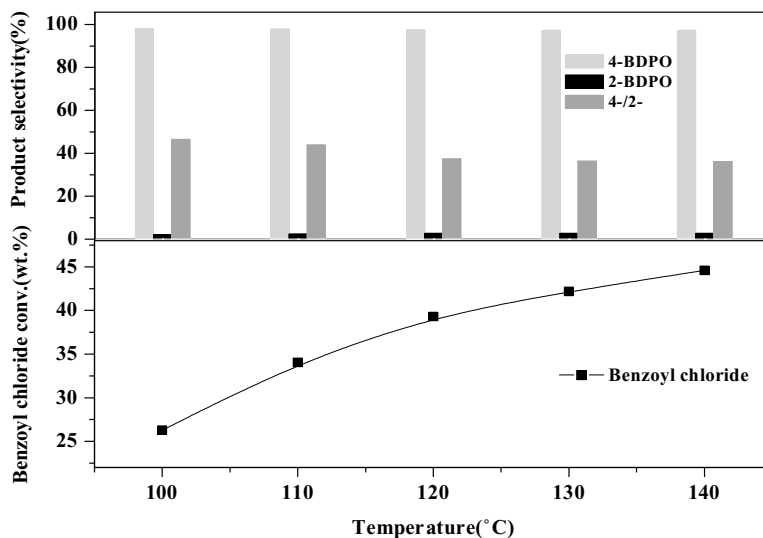


Fig. 1. Effect of reaction temperature. Conditions: catalyst = 15 wt.% TPA/ZrO₂, catalyst wt. = 0.15 g (3 wt.% of the reaction mixture), wt. of reaction mixture = 5 g, (DPO/BC) molar ratio = 7:1, time = 3 h.

conditions the same. As DPO/BC molar ratio is increased from 1 to 15, conversion of BC increased linearly with no change in the product distribution and gave highest selectivity for 4-(benzoyl) DPO.

3.7. Effect of catalyst concentration in the benzoylation of DPO by BC

To know the effect of 15 wt.% TPA/ZrO₂ catalyst concentration on the conversion of BC and product distribution in the benzoylation of DPO, the reaction was conducted by changing the catalyst concentration in the range 1–5 wt.%

of total reaction mixture (5 g), keeping constant molar ratio of DPO:BC as 7, 120 °C and 3 h. The results are shown in Fig. 3 as a conversion of benzoyl chloride as a function of catalyst concentration. It is seen from the graph that the conversion of BC increased from 26 to 45% linearly in 3 h, giving highest selectivity for 4-(benzoyl)-DPO (>97%).

3.8. Time on stream study

In order to study the effect of time on stream, benzoylation reaction was studied as a function of time under optimized conditions and the results are shown in Fig. 4.

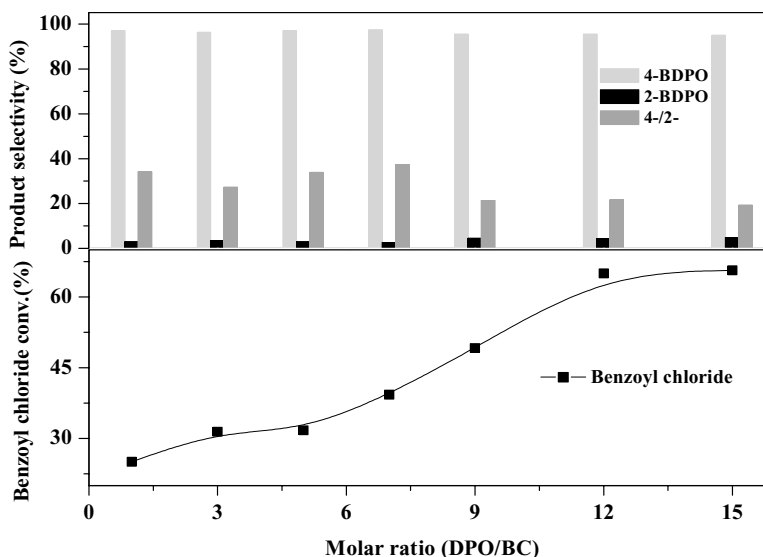


Fig. 2. Effect of diphenyl oxide to benzoyl chloride molar ratio. Conditions: catalyst = 15 wt.% TPA/ZrO₂, catalyst wt. = 0.15 g (3 wt.% of the reaction mixture), wt. of reaction mixture = 5 g, temperature = 120 °C, time = 3 h.

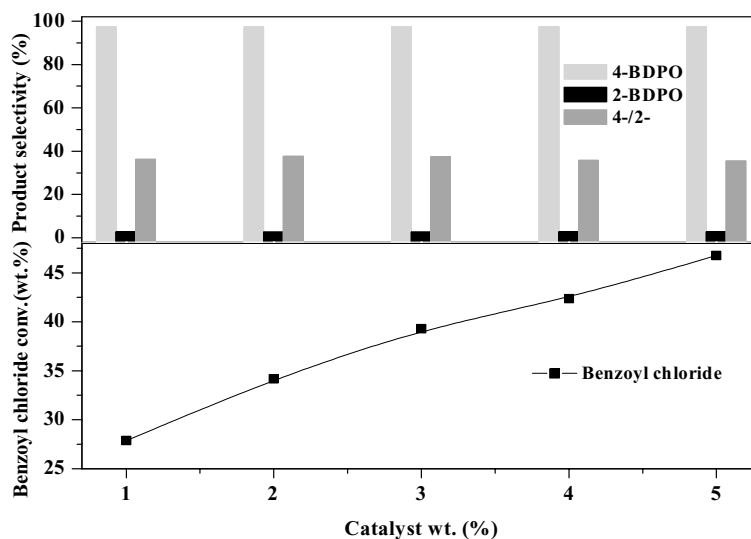


Fig. 3. Effect of catalyst concentration. Conditions: catalyst = 15 wt.% TPA/ZrO₂, wt. of the reaction mixture = 5 g, temperature = 120 °C, (DPO/BC) molar ratio = 7:1, time = 3 h.

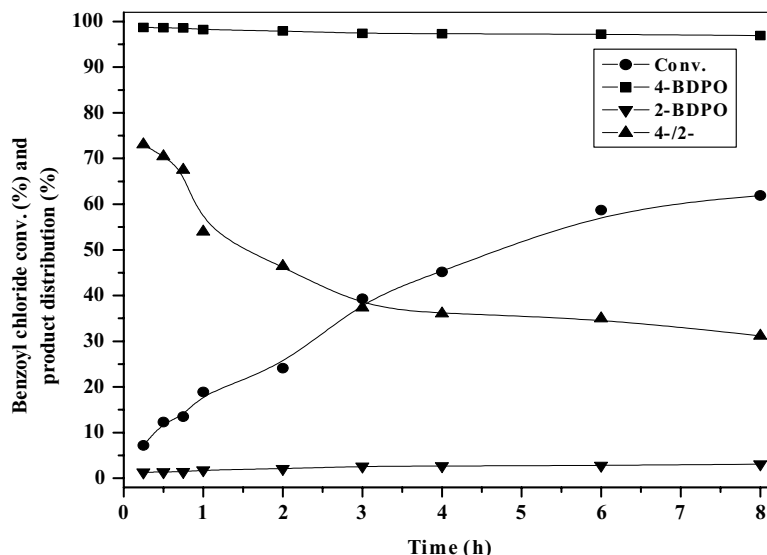


Fig. 4. Study of time on stream. Conditions: catalyst = 15 wt.% TPA/ZrO₂, catalyst wt. = 0.15 g (3 wt.% of the reaction mixture), wt. of reaction mixture = 5 g, temperature = 120 °C, (DPO/BC) molar ratio = 7:1.

Conversion of BC was almost linearly increased with increase in time, while *o*- and *p*-selectivities with highest selectivity for *para* product in the benzylation reaction remains the same through out the reaction.

3.9. Recyclability of the catalyst

For knowing the recyclability of the catalyst, the catalyst used in the first cycle was removed by filtration, washed three times with AR grade 1,2-dichloromethane and dried in an oven for overnight at 100 °C. The catalyst is then activated at 500 °C for 4 h in airflow. The above procedure was repeated in one more cycle and the catalytic activity (conversion of BC) is presented in Table 3. From the results it is concluded that even after 2nd cycle there was no consider-

able loss in the catalytic activity indicated by the conversion of BC.

4. Conclusions

Benzylation of DPO with BC was carried out over 15 wt.% TPA/ZrO₂ catalyst calcined at 750 °C in liquid phase conditions. The catalyst with 15 wt.% loading showed highest catalytic activity at 120 °C with DPO:BC molar ratio 7 and 3 wt.% catalyst concentration (of the total reaction mixture). Under the above optimized conditions, TPA/ZrO₂ showed good catalytic activity and shape selectivity to 4-(benzoyl) DPO (97.4%) with a maximum conversion of benzoyl chloride (39.3%) at 120 °C. The above catalyst was

recyclable, cost effective and environmental friendly and could be used in similar reactions.

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