



# Single step synthesis of 4-hydroxybenzophenone via esterification and Fries rearrangement: Novelty of cesium substituted heteropoly acid supported on clay

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## ARTICLE INFO

### Article history:

Received 26 September 2007  
Received in revised form 15 April 2008  
Accepted 21 April 2008  
Available online 30 April 2008

### Keywords:

Esterification  
Fries rearrangement  
Friedel–Crafts acylation  
Heteropoly acids  
Clay

## ABSTRACT

Hydroxybenzophenones are important precursors used in fine chemical and pharmaceutical industries. The esterification reaction of phenol with benzoic acid, followed by the Fries rearrangement towards hydroxybenzophenones in a one-pot liquid phase operation was examined with several catalysts under solvent-free conditions. Cesium substituted dodecatungstophosphoric acid supported on K-10 clay (designated as  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$ ) was found to be the most active and selective catalyst towards 4-hydroxybenzophenone in comparison with others. The order of activity was as follows: 20% w/w  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$  (most active)  $\sim$  (almost equal)  $\text{UDCaT-5}$  > 20% w/w  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{HMS}$  >  $\text{UDCaT-6}$  (least).

The conversion of benzoic acid and selectivity for 4-hydroxybenzophenone at a phenol to benzoic acid mole ratio of 7:1, using 0.05 g/cm<sup>3</sup>  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$  at 200 °C were 70% and 32.5%, respectively. The effects of various reaction parameters on the rate of reaction and selectivity were investigated.

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## 1. Introduction

Catalysis plays a pivotal role in adoption of Green Chemistry. Solid acid catalysts have attracted much attention in recent years in fine chemicals and pharmaceuticals because the traditional homogeneous acid catalyzed processes of fine chemicals produce large amount of pollutants and need to be replaced by environmentally friendly processes. Solid acid catalysts are non-corrosive and reusable and can be used in a variety of reactor configurations and modes to reduce reactor volume and processing times resulting into process intensification; and thus the resultant catalytic processes promote green technology.

The Friedel–Crafts aromatic acylation and related Fries rearrangement of aryl esters are the most important routes for the synthesis of hydroxyl aromatic ketones such as hydroxybenzophenones that are intermediates in manufacturing of fine and speciality chemicals as well as pharmaceuticals. Current industrial practices in these operations involve use of over-stoichiometric amounts of Lewis acids such  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ , and Bronsted acids such as HF,  $\text{H}_2\text{SO}_4$ , etc. as catalysts, which results in a formation of substantial amount of by-products and corrosion problems [1].

Benzophenone and its derivatives have been widely used as sources of chemical synthesis, ultraviolet protection products, and cosmetic ingredients for ultraviolet absorption. Derivatives of benzophenone are also contained in natural foods such as mangosteen [2]. Hydroxybenzophenones are intermediates for dyes, pharmaceuticals, and perfumeries. They are also used as UV absorbers in polymers. 4-Hydroxybenzophenone (HBP) is an intermediate for the synthesis of tamoxifen, the archetypal selective estrogen receptor modulator (SERM), which is the drug most used to combat breast cancer [3]. It is also an intermediate for the synthesis of clomiphene citrate, an ovulation stimulant in human female [4].

Fries rearrangement of phenyl benzoate has been demonstrated using a variety of solid acid catalysts. Published literature provides an account of the various factors which influence the conversion and selectivity of this reaction. incorporated. The use of zeolites in Fries rearrangement is promising [5–7], but the selectivity and reactivity of zeolites need to be improved and rapid deactivation of catalysts need to be overcome before they are commercialized. Olah et al. [8] tested Nafion-H as a catalyst for the Fries rearrangement of phenyl benzoate whereas Kozhevnikova et al. [9] reported it with cesium substituted heteropoly acid as catalyst. The selectivity of several zeolites has been compared in a direct Fries reaction of phenol with benzoic anhydride to 4-HBP to follows an order [10]: H-beta (maximum) > H-Y > RE-Y >  $\text{AlCl}_3$  > H-mordenite  $\approx$  H-ZSM-5 (minimum). H-beta showed the

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**Nomenclature**

$a_p$	solid–liquid interfacial area ( $\text{cm}^2/\text{cm}^3$ of liquid phase)
$A$	benzoic acid
$A_i$	pre-exponential factor ( $i = 1, 2, 3$ and 2–3 reaction)
$B$	phenol
$C_A$	concentration of A ( $\text{mol}/\text{cm}^3$ )
$C_{A0}$	initial concentration of A at solid (catalyst) surface ( $\text{mol}/\text{cm}^3$ )
$C_B$	concentration of B ( $\text{mol}/\text{cm}^3$ )
$C_{B0}$	initial concentration of B in bulk liquid phase ( $\text{mol}/\text{cm}^3$ )
$C_{WP}$	Wiesz–Prater parameter
$D_{AB}$	diffusion coefficient of A in B ( $\text{cm}^2/\text{s}$ )
$D_{BA}$	diffusion coefficient of B in A ( $\text{cm}^2/\text{s}$ )
$D_e$	effective diffusivity of benzoic acid ( $\text{cm}^2/\text{s}$ )
$E_i$	activation energy of $i$ th route ( $i = 1, 2, 3$ and 2–3)
$k_1$	reaction rate constant for forward esterification reaction
$k'_1$	surface reaction rate constant for reverse reaction
$k_2$	reaction rate constant for acylation reaction to 2-hydroxybenzophenone
$k_{1-2}$	reaction rate constant for Fries reaction of phenyl benzoate to 2-hydroxybenzophenone
$k_3$	reaction rate constant for acylation reaction to 4-hydroxybenzophenone
$k_{2-3}$	esterification equilibrium constant, $k_{2-3}/k'_{2-3}$
$k_{2-3}$	forward rate constant for isomerisation of 2-hydroxybenzophenone to 4-hydroxybenzophenone
$k'_{2-3}$	reverse rate constant for isomerisation of 4-hydroxybenzophenone to 2-hydroxybenzophenone
$K_1$	esterification equilibrium constant $k_1/k'_1$ (route 1)
$r_{\text{obs}}$	overall rate of reaction based on liquid phase volume ( $\text{mol cm}^{-3} \text{s}^{-1}$ )
$r_{2\text{-HBP}}$	net rate of formation of 2-hydroxybenzophenone
$r_{4\text{-HBP}}$	net rate of formation of 4-hydroxybenzophenone
$r_{\text{PhOBz}}$	net rate of formation of phenyl benzoate
$R_p$	radius $r$ of catalyst particle (cm)
$Sh$	sherwood number
$S_{4\text{-HBP}}$	selectivity to 4-hydroxybenzophenone
<b>Greek letters</b>	
$\varepsilon$	catalyst porosity
$\tau$	tortuosity
$\rho_p$	density of catalyst particle ( $\text{g}/\text{cm}^3$ )

highest selectivity of 23.3% towards 4-HBP after 20 h, at 220 °C, with a mole ratio of benzoic anhydride: phenol of 1:20. The requirements of high temperature, high mole ratio, low selectivity and long reaction time render the foregoing process highly energy intensive and uneconomical.

A novel strategy to minimize waste in this type of reaction should be the esterification and the Fries rearrangement with the same regenerable catalyst in a single pot operation under solvent-free conditions. Such a strategy was adopted and the reaction between phenol and benzoic acid was investigated by using various solid acid catalysts. The results of the direct and clean Fries reaction are reported in this paper together with the effects of different parameters on product profile in order to get insight into the reaction mechanism. Direct Fries rearrangement of phenyl benzoate was also studied to throw light on the reaction pathway.

**2. Experimental****2.1. Chemicals and catalysts**

The following chemicals were procured from firms of repute and used without further purification: phenol, benzoic acid, zirconium oxychloride, aqueous ammonia solution, cesium chloride, dodecatungstophosphoric acid (sd Fine Chem. Ltd., Mumbai, India), hexadecyl amine, chlorosulfonic acid (Spectrochem. Ltd., Mumbai, India), tetraethyl orthosilicate, K-10 clay (Fluka, Germany). Hexagonal mesoporous silica (HMS) was prepared by a procedure described elsewhere [11]. The catalysts used for the reaction were dried at 120 °C for 3 h before use.

**2.1.1. Preparation of  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$** 

Approximately 10 g of K-10 was dried in an oven to 120 °C for 1 h of which 8 g were weighed accurately. 0.2808 g ( $1.671 \times 10^{-3}$  mol) of CsCl was weighed accurately and dissolved in 10 ml of methanol. This volume of solvent used was approximately equal to the pore volume of the catalyst. The solution was added to the previously dried and accurately weighed 8 g of K-10 clay to form slurry. The slurry was stirred vigorously and air-dried. The resulted material was then dried in an oven at 120 °C for 2 h. This was then further subjected to impregnation by an alcoholic solution of 2 g ( $6.688 \times 10^{-4}$  mol) of DTP in 10 ml of methanol. The solution was added to the previously treated K-10 clay with CsCl again to form slurry. The slurry was stirred vigorously and air-dried. The pre-formed catalyst was dried in an oven at 120 °C for 2 h and then calcined at 300 °C for 3 h [12–15].

**2.1.2. Preparation of UDCaT-5**

UDCaT-5 was prepared by adding aqueous ammonia solution to zirconium oxychloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) solution at a pH of 9–10. The precipitated zirconium hydroxide so obtained was washed with deionized water until a neutral filtrate was obtained. The absence of chlorine ion was detected by the  $\text{AgNO}_3$  test. A material balance on chloride ions before and after precipitation and washing shows no retention of  $\text{Cl}^-$  on the solid. Zirconium hydroxide was dried in an oven for 24 h at 100 °C and was crushed to 100 mesh size.  $\text{Zr}(\text{OH})_4$  was then added to a solution containing 15  $\text{cm}^3/\text{g}$  of 0.5 M chlorosulfonic acid in ethylene dichloride and agitated with a glass rod. The material was left for 5 min in the solution under careful moisture-free condition and kept in an oven as such, and the heating was started slowly to 120 °C after about 30 min. The material was kept in oven at 120 °C for 24 h and calcined at 650 °C for 3 h to get the active catalyst UDCaT-5 [16,17].

**2.1.3. Preparation of UDCaT-6**

The series of catalysts in UDCaT stand for the acronym University Department of Chemical Technology. 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  $\text{AgNO}_3$  test. It was further dried in an oven for 2 h at 120 °C.  $\text{Zr}(\text{OH})_4/\text{HMS}$  was immersed in 15  $\text{cm}^3/\text{g}$  of 0.5 M chlorosulfonic acid in ethylene dichloride. It was soaked for 5 min in the solution and then without allowing any moisture absorption, it was oven-dried to evaporate the solvent at 120 °C for 30 min. The sample was then kept in the oven at 120 °C for further 24 h and calcined thereafter at 650 °C for 3 h to the final solid catalyst called UDCaT-6 [18].

### 2.1.4. Preparation of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{HMS}$

10 g of precalined HMS was dried in oven at 120 °C for 3 h of which 8 g were weighed accurately. 0.2808 g ( $1.671 \times 10^{-3}$  mol) of CsCl was weighed accurately and dissolved in 10 ml of methanol. This volume of solvent used was approximately equal to the pore volume of the catalyst. The solution was added in small aliquots of 1 ml each time to the silica molecular sieve with constant stirring with a glass rod or kneading it properly. The solution was added at time intervals of 2 min. Initially on addition of the CsCl solution to HMS was in powdery form but on complete addition it formed a paste. The paste on further kneading for 10 min resulted in a free flowing powder. The resulted material was dried at 120 °C for 3 h for the removal of solvents. This then was further subjected to impregnation by an alcoholic solution of 2 g ( $6.688 \times 10^{-4}$  mol) of DTP in 10 ml of methanol. The solution was added to the treated HMS by following the above procedure. The preformed material was dried in an oven at 120 °C for 3 h and then calcined at 300 °C for 3 h. The catalyst was found to possess highest activity when calcined at above-mentioned temperature.

### 2.2. Reaction procedure

All reactions were carried out in a 100 cm<sup>3</sup> stainless steel Parr autoclave reactor with an internal diameter of 5 cm. A standard four pitched blade turbine impeller was used for agitation. The temperature was maintained at  $\pm 1$  °C of the desired value. In a typical reaction, 0.28 mol of phenol and 0.04 mol of benzoic acid were taken. Chlorobenzene was used as an internal standard (1.2 g) with a catalyst loading of 0.05 g/cm<sup>3</sup>. The reaction was carried out without solvent. The catalysts were dried at 120 °C for 3 h before use. The reaction mixture was allowed to reach the desired temperature and the initial sample was collected. Agitation was then commenced at a known speed. Samples were withdrawn at periodic intervals up to 3 h.

The reaction scheme is as shown below:

In order to understand the mechanism and product profile, Fries rearrangement of phenyl benzoate was studied independently. 0.004 mol of phenyl benzoate was made up to 35 cm<sup>3</sup> with chlorobenzene as solvent, at a catalyst loading of 0.05 g/cm<sup>3</sup> and temperature was 200 °C in the autoclave under autogenous pressure. The catalysts were dried at 120 °C for 3 h before use. The reaction mixture was allowed to reach the desired temperature and the initial sample was collected. Agitation was then commenced at a known speed. Samples were withdrawn at periodic intervals up to 3 h.

### 2.3. Analysis

Analysis of the reaction mixture was performed by gas chromatography (Chemito Model 1000, FID detector) using a BP1 capillary column (0.22 mm  $\times$  25 m). The products were confirmed by GC-MS (PerkinElmer Clarius Model 500) by using BPX-1 capillary column (0.25 mm  $\times$  30 m) packed with methyl polysiloxane.

## 3. Results and discussion

### 3.1. Efficacies of various catalysts

Various solid acid catalysts were used to assess their efficacy in this single pot reaction. A 0.05 g/cm<sup>3</sup> loading of catalyst based on the volume of the reaction mixture was employed at 200 °C and a speed of agitation of 800 rpm.

The reaction is shown in Scheme 1. The reaction proceeds through formation of a carbocation from benzoic acid (phenylacylonium ion) ( $\text{PhCO}^+$ ) by abstraction of water and it undergoes

three parallel reactions leading to the formation of phenyl benzoate (**1**) (route 1, esterification reaction, equilibrium reaction,  $K_1 = \frac{k_1}{k_1^-}$ ), direct acylation to 2-hydroxybenzophenone (**2**) (route 2, rate constant  $k_2$ ), and to 4-hydroxybenzophenone (**3**) (route 3, rate constant  $k_3$ ), and in situ Fries rearrangement of phenyl benzoate to 2-hydroxybenzophenone (route 4, rate constant,  $k_{1-2}$ ), and isomerization of 2-hydroxybenzophenone to 4-hydroxybenzophenone (route 5, equilibrium constant  $K_{2-3} = \frac{k_{2-3}}{k_{2-3}^-}$ ). This would suggest that it is a complex reaction network and the values of the rates of reactions of individual reactions will govern the overall product profile. Thus, the mole ratio, catalyst loading and temperature will have significant role apart from the nature and strength of acidity and pore size distribution.

Therefore, UDCaT-5, 20% (w/w)  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$ , 20% (w/w)  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{HMS}$ , and UDCaT-6 were selected as the catalysts. Table 1 summarizes the results which are most interesting from the following perspectives. The order of activity was as follows:

20% w/w  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$  (most active and selective)  
 $\sim$  (almost equal) UDCaT-5 > 20% w/w  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/$   
 HMS > UDCaT-6 (least).

However, the selectivities are different and are as follows.

#### 3.1.1. Selectivity to phenyl benzoate

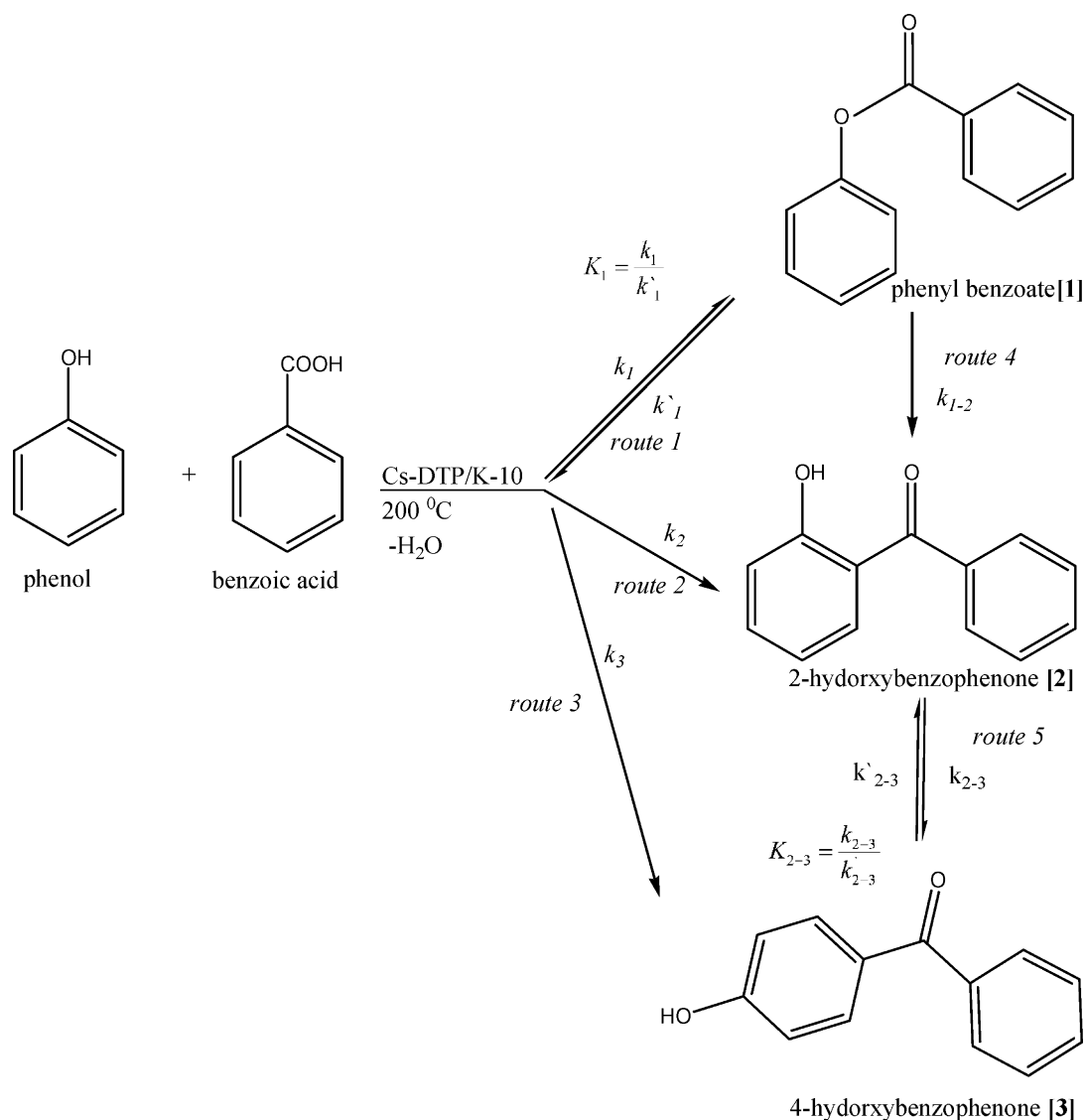
UDCaT-6 (most active and selective) > 20% w/w  
 $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{HMS}$  > UDCaT-5 > 20% w/w  
 $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$  (least).

If phenyl benzoate is the desired product then UDCaT-6 is the best catalyst, which does not promote in situ Fries rearrangement to 2-hydroxybenzophenone subsequently. UDCaT-6 and UDCaT-5 catalysts are more acidic and the esterification followed by rearrangement with release of water deactivates the catalyst in comparison with the cesium substituted heteropoly acid which is water tolerant [13–17].

#### 3.1.2. Selectivity to 4-hydroxybenzophenone

20% w/w  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$  (most active) > UDCaT-5 >  
 20% w/w  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{HMS}$  > UDCaT-6 (least).

The selectivity to 4-hydroxybenzophenone will increase if all of the following reactions are promoted: (i) the reverse reaction in esterification (route 1), (ii) Fries rearrangement reaction to 2-hydroxybenzophenone (route 4), (iii) followed by isomerisation to 4-hydroxybenzophenone (route 5) and (iv) direct acylation (route 3, rate constant  $k_3$ ). The equilibrium constant  $K_{2-3}$  should be very high and thus temperature plays an important role. The role of support is also important here. K-10 is an acid treated clay whereas HMS is an inert support. The role of K-10 in synergism with heteropoly acids was reported for the first time in some of our earlier works [19–21]. K-10 has a narrow pore sizes in comparison with mesopores in HMS. 4-Hydroxybenzophenone is a slimmer molecule than 2-hydroxybenzophenone and hence the selectivity is enhanced with  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$  catalyst.



**Scheme 1.** Product profile for esterification and Fries rearrangement.

$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$  showed excellent activity and highest selectivity to 32.5% towards 4-hydroxybenzophenone in comparison with the rest, which is much better than zeolites studied by Chaube et al. [10]. Acid treated K-10 clay supported  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  is more stable and active at higher temperatures than  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  as a catalyst for Fries rearrangement. Further experiments were conducted with  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$  due to its excellent stability and reusability at higher temperature. A brief characterization of this catalyst is presented.

**Table 1**  
Efficacies of various catalysts<sup>a</sup>

Catalyst	Conversion of benzoic acid (%)	Selectivity (%)		
		Phenyl benzoate	4-HBP	2-HBP
Cs-DTP <sup>b</sup> /K-10	70	49.5	32.5	18
UDCaT-5	67	62	18	20
Cs-DTP <sup>b</sup> /HMS	52	75	15	10
UDCaT-6	46	87	11	2

<sup>a</sup> Speed of agitation 800 rpm, phenol 0.28 mol, benzoic acid 0.04 mol, catalyst loading 0.05 g/cm<sup>3</sup>, temperature 200 °C and time 3 h.

<sup>b</sup> Cs-DTP = 20% (w/w)  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  on the given support.

### 3.2. Characterization of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$

The catalyst was fully characterized, and the details are reported by us [13,14]. Only a few salient features are reported here. Crystallinity and textural patterns of the catalysts obtained from X-ray diffractograph of  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$  show that DTP is crystalline while K-10 is amorphous. Although the  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  salt had lost some of its crystallinity when supported on K-10, the Keggin structure of DTP remained intact. The FT-IR analysis also confirmed the preservation of the Keggin structure. Bulk DTP ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) and  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  show the characteristic IR bands at ca 1080 cm<sup>-1</sup> (P–O in central tetrahedral), 984 cm<sup>-1</sup> (terminal W=O) 897 cm<sup>-1</sup> and 812 cm<sup>-1</sup> (W–O–W) associated with the asymmetric vibrations in the Keggin polyanion. However,  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  is characterized by a split in the W=O band, suggesting the existence of direct interaction between the polyanion and Cs<sup>+</sup>. FT-IR of 20% (w/w) DTP/K-10 and 20% (w/w)  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$  indicate that the primary Keggin structure is preserved in both the cases on K-10 support. The bands in the region of 1600–1700 cm<sup>-1</sup> (at 1631–1642 cm<sup>-1</sup>) are attributed to –OH bending frequency of water molecules

present in catalysts. In case of DTP, it is present as water of crystallization, while in case of  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ , it indicates the presence of partial  $\text{H}^+$  ion directly attached to the polyanion ( $-\text{O}-\text{H}$ ) and is present in K-10 as  $\text{M}-\text{OH}$  and possibly as  $\text{H}_3\text{O}^+$  [13,14]. The scanning electron micrographs reveal that both K-10 and 20% (w/w) DTP/K-10 samples possess rough and rugged surfaces. On the contrary 20% (w/w)  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ /K-10 shows a smoother surface because of a layer of  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  over the external surface of K-10. The Brunauer–Emmett–Teller surface area of 20% (w/w)  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ /K-10 was measured to be  $207\text{ m}^2\text{ g}^{-1}$ , and the pore volume and pore diameter were  $0.29\text{ cm}^3/\text{g}$  and  $58\text{ \AA}$ , respectively. The adsorption–desorption isotherm for  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ /K-10 showed that it was type IV isotherm with a hysteresis loop of type H3, which is a characteristic of a mesoporous solid.

### 3.3. Effect of speed of agitation

The effect of speed of agitation was studied in the range of 600–1000 rpm at a catalyst loading  $0.05\text{ g/cm}^3$  at  $200^\circ\text{C}$  (Fig. 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 benzoic acid to the external surface of the catalysts. All further reactions were carried out at a speed of 800 rpm. Theoretical calculations were also done to establish that there was absence of external mass transfer resistance. A complete theory is given elsewhere by us [22,23] and a typical calculation is presented here for the sake of brevity.

The rate of mass transfer could be calculated from the knowledge of mass transfer coefficients for both the reactants, which were obtained from their bulk liquid phase diffusivities. The liquid phase diffusivity values  $D_{\text{AB}}$  (benzoic acid in phenol) and  $D_{\text{BA}}$  (phenol in benzoic acid) were calculated by using Wilke–Chang equation. The values of  $D_{\text{AB}}$  and  $D_{\text{BA}}$  at 473 K were calculated as  $1.19 \times 10^{-4}$  and  $6.73 \times 10^{-5}\text{ cm}^2/\text{s}$ , respectively. The values of solid–liquid mass transfer coefficients  $k_{\text{SL-A}}$  and  $k_{\text{SL-B}}$  were calculated by the Sherwood number correlation as  $4.79 \times 10^{-2}$  and  $2.70 \times 10^{-2}\text{ cm/s}$ , respectively. To be on the safer side, the limiting

value of the Sherwood number was taken as two. The actual value is so far greater than two due to intense agitation [22,23].

The surface area of particles per unit liquid volume was calculated for  $50\text{ }\mu\text{m}$  particle size (average) at a catalyst loading of  $0.05\text{ g/cm}^3$ . Thus the values of mass transfer rates of benzoic acid ( $=k_{\text{SL-A}}a_pC_{\text{A0}}$ ) and phenol ( $=k_{\text{SL-B}}a_pC_{\text{B0}}$ ) from the bulk liquid of the external surface of the catalyst, were found to be  $4.31 \times 10^{-3}$  and  $1.69 \times 10^{-3}\text{ mol/cm}^3\text{ s}$ , respectively at A:B mole ratio of 1:7. The initial observed rate of the reaction was found to be  $2.04 \times 10^{-6}\text{ mol/cm}^3\text{ s}$ . It confirms that the mass transfer rates were much higher than the 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  $0.01\text{--}0.07\text{ g/cm}^3$  (Fig. 2). In the absence of external mass transfer resistance, the rate of reaction was directly proportional to catalyst loading based on the entire liquid phase volume. This indicates that as the catalyst loading increased the conversion of benzoic acid increases, which is due to proportional increase in the number of active sites. However, beyond a catalyst loading of  $0.05\text{ g/cm}^3$ , there was no significant increase in the conversion and hence all further experiments were carried out at this catalyst loading.

### 3.5. Proof of absence of intra-particle diffusion resistance

The Weisz–Prater criterion was employed to assess the influence of intra-particle diffusion resistance [24]. According to Weisz–Prater criterion, the dimensionless parameter  $\{C_{\text{wp}} = r_{\text{obs}}\rho_p R_p^2/D_e[C_{\text{A0}}]\}$  which represents the ratio of the intrinsic reaction rate to the intra-particle diffusion rate, can be evaluated from the observed rate of reaction, the particle radius ( $R_p$ ), effective diffusivity of the limiting reactant ( $D_e$ ) and concentration of the reactant at the external surface of the particle. The effective diffusivity of benzoic acid ( $D_{e-A}$ ) inside the pores of the catalyst was obtained from the bulk diffusivity ( $D_{\text{AB}}$ ), porosity ( $\varepsilon$ ) and tortuosity

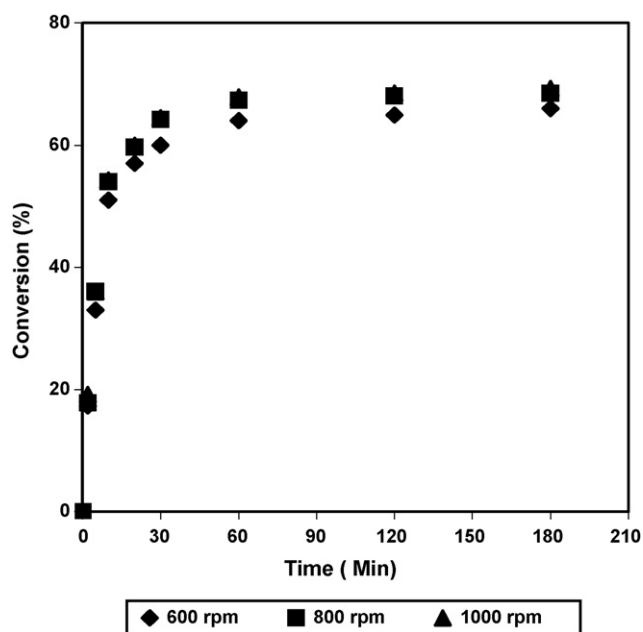


Fig. 1. Effect of speed of agitation on conversion of benzoic acid. Phenol, 0.28 mol; benzoic acid 0.04 mol; catalyst loading  $0.05\text{ g/cm}^3$ ; temperature  $200^\circ\text{C}$ .

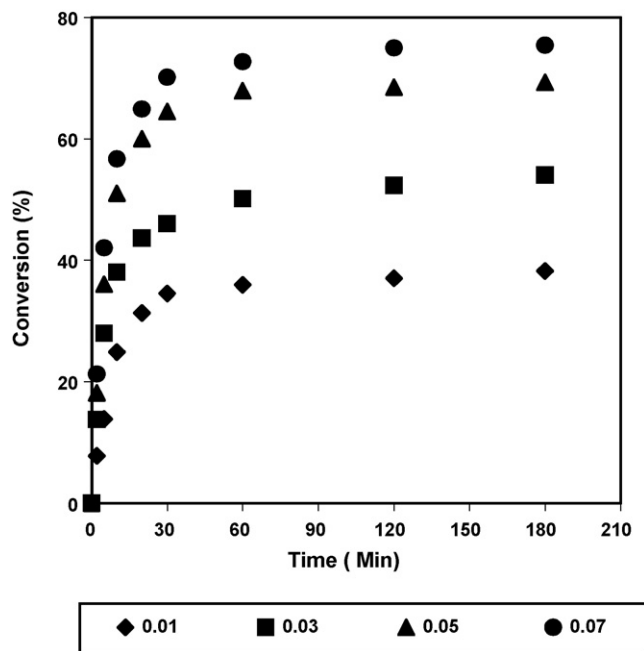


Fig. 2. Effect of catalyst loading (in  $\text{g/cm}^3$ ) on conversion of benzoic acid. Speed of agitation 800 rpm; phenol 0.28 mol; benzoic acid 0.04 mol; temperature  $200^\circ\text{C}$ .



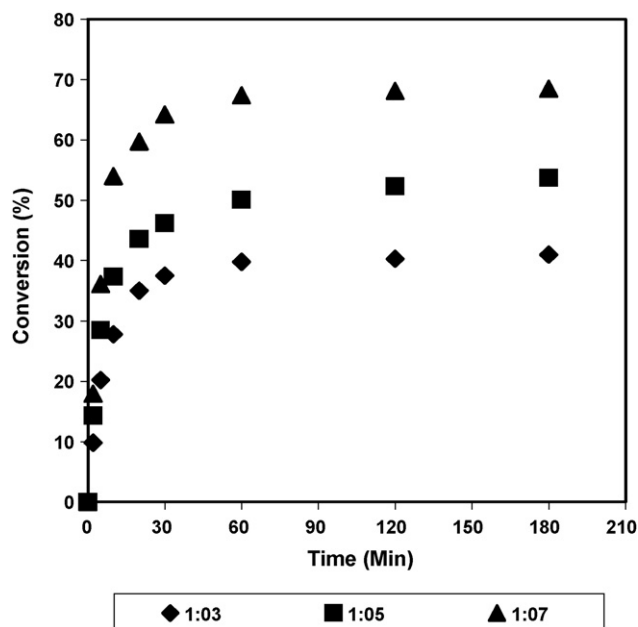


Fig. 3. Effect of mole ratio of benzoic acid to phenol on conversion of benzoic acid. Speed of agitation 800 rpm; catalyst loading 0.05 g/cm<sup>3</sup>; temperature 200 °C.

( $\tau$ ) as  $8.98 \times 10^{-6}$  cm<sup>2</sup>/s where  $D_{e-B} = D_{AB} \varepsilon / \tau D_{AB}$  was obtained from the Wilke–Chang equation [26]. The average values of porosity and tortuosity were taken as 0.4 and 3, respectively as a conservative estimate [24]. In the present case, the value of  $C_{wp}$  was calculated as  $4.84 \times 10^{-3}$ , which was less than 1, and it proved that there was no intra-particle diffusion resistance.

### 3.6. Effect of mole ratio

The effect of benzoic acid to phenol mole ratio was studied at 1:3, 1:5 and 1:7 by keeping the catalyst loading constant. The conversion of benzoic acid was found to increase with an increase in concentration of phenol (Fig. 3). Selectivity towards 4-hydroxybenzophenone was also found to increase with an increase in concentration of phenol (Fig. 4). Lassila et al. [25] have reported that enhancement of

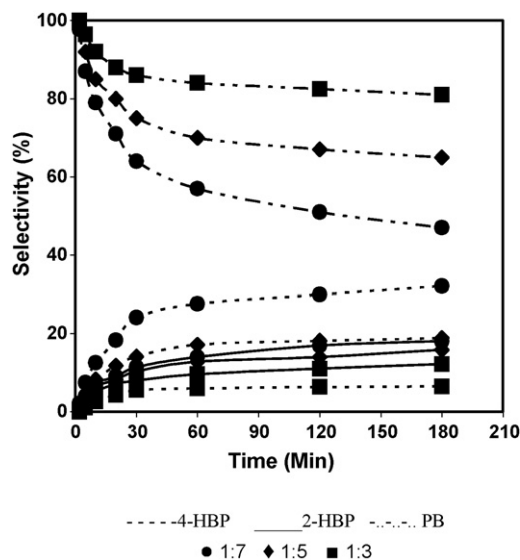


Fig. 4. Effect of mole ratio of benzoic acid to phenol on selectivity. Speed of agitation 800 rpm; catalyst loading 0.05 g/cm<sup>3</sup>; temperature 200 °C.

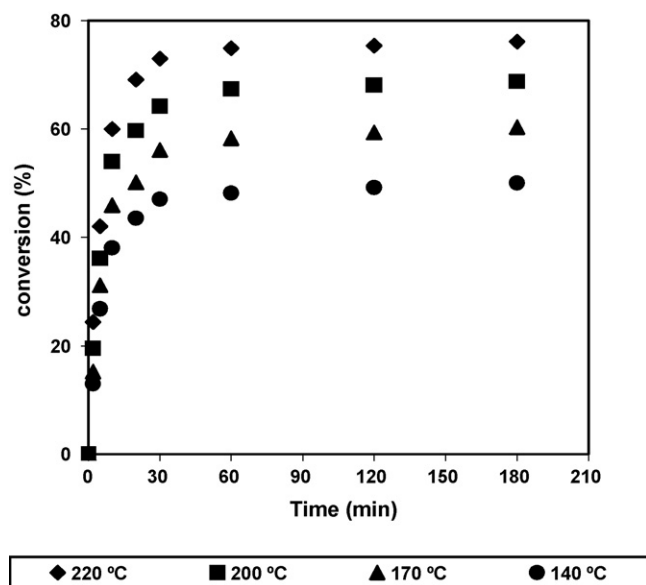


Fig. 5. Effect of temperature on conversion of benzoic acid. Speed of agitation 800 rpm; phenol 0.28 mol; benzoic acid 0.04 mol; catalyst loading 0.05 g/cm<sup>3</sup>.

phenol concentration increases *para* selectivity in Fries rearrangement of phenyl benzoate. Therefore, all further experiments were studied by keeping a high benzoic acid:phenol mole ratio of 1:7.

### 3.7. Effect of temperature

The effect of temperature on conversion and selectivity was studied under otherwise similar conditions at 140, 170, 200 and 220 °C, respectively. It was observed that the conversion of benzoic acid (Fig. 5) and selectivity towards 4-hydroxybenzophenone (Fig. 6) were increased with an increase in temperature. This would

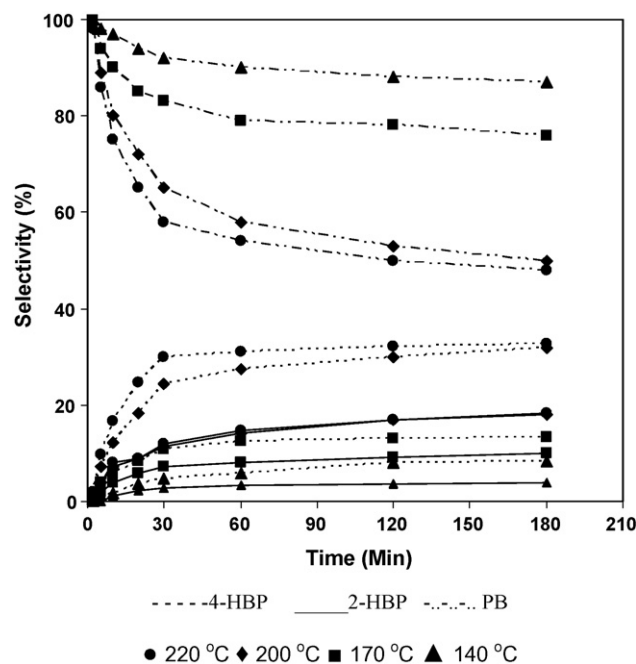


Fig. 6. Effect of temperature on selectivity of various products. Speed of agitation 800 rpm; phenol 0.28 mol; benzoic acid 0.04 mol; catalyst loading 0.05 g/cm<sup>3</sup>.

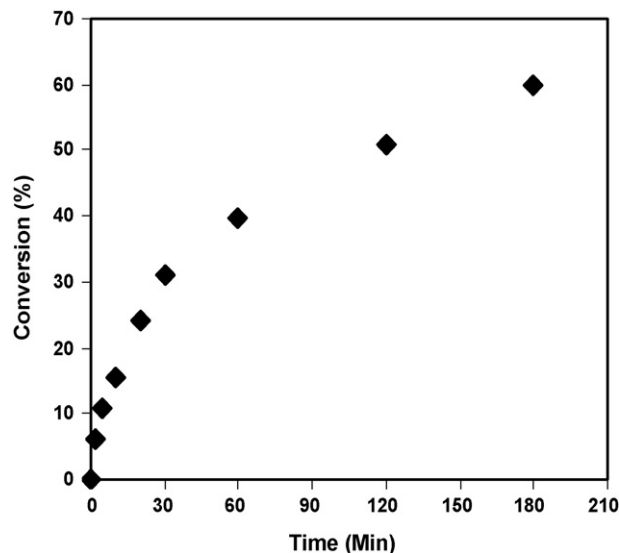
**Table 2**  
Reusability of 20% (w/w) Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub>/K-10<sup>a</sup>

Run no.	Conversion of benzoic acid (%)	Selectivity (%)		
		Phenyl benzoate	4-HBP	2-HBP
Fresh <sup>b</sup>	70	49.5	32.5	18
1st run <sup>b</sup>	63.8	51	31.8	16.8
2nd run <sup>b</sup>	58.0	52	31.1	16.5
3rd run <sup>c</sup>	69.7	49.3	32.4	18.2

<sup>a</sup> Speed of agitation 800 rpm, phenol 0.28 mol, benzoic acid 0.04 mol, catalyst loading 0.05 g/cm<sup>3</sup> (fresh and 3rd run), temperature 200 °C, time 3 h.

<sup>b</sup> No make-up catalyst.

<sup>c</sup> Make-up catalyst.



**Fig. 7.** Direct Fries rearrangement of phenyl benzoate. Speed of agitation 800 rpm; temperature 200 °C; catalyst loading 0.05 g/cm<sup>3</sup>; phenyl benzoate 0.004 mol.

suggest a kinetically controlled mechanism. The forward constants  $k_3$  (direct acylation to 4-hydroxybenzophenone) and  $k_{2-3}$  (isomerisation) are strongly temperature dependent and the corresponding activation energy values are much higher in comparison those  $k_2$  (direct acylation to 2-hydroxybenzophenone) and  $k_{1-2}$  (Fries rearrangement) for the formation of 2-hydroxybenzophenone and therefore with increase in temperature the selectivity increases to 4-hydroxybenzophenone from 140 to 200 °C.

Selectivity to 4-HBP is given by the net rate of formation of 4-HBP to that of rest of the products and is

$$\begin{aligned}
 S_{4\text{-HBP}} &= \frac{r_{4\text{-HBP}}}{r_{\text{PhOBz}} + r_{2\text{-HBP}}} \\
 &= \frac{k_3 [\text{PhOH}] [\text{PhCOOH}] + k_{2-3} [2\text{-HBP}]}{k_1 [\text{PhOH}] [\text{PhCOOH}] + k_2 [\text{PhOH}] [\text{PhCOOH}] - k_{2-3} [2\text{-HBP}]} \\
 &= \frac{1 + k_{2-3} [2\text{-HBP}] / k_3 [\text{PhOH}] [\text{PhCOOH}]}{k_1 + k_2 / k_3 - k_{2-3} [2\text{-HBP}] / k_3 [\text{PhOH}] [\text{PhCOOH}]} \\
 &= \frac{1 + (A_{23}/A_3) e^{-(E_{23}-E_3)/RT} ([2\text{-HBP}] / [\text{PhOH}] [\text{PhCOOH}])}{(A_1/A_3) e^{-(E_1-E_3)/RT} + (A_2/A_3) e^{-(E_2-E_3)/RT} - (A_{23}/A_3) e^{-(E_{23}-E_3)/RT} ([2\text{-HBP}] / [\text{PhOH}] [\text{PhCOOH}])}
 \end{aligned}$$

This equation shows that at a given temperature, higher the value of  $E_{23}$ , greater will be the selectivity at a given concentration of phenol and benzoic acid. As the temperature is increased, selectivity increases. When there is no formation of 2-HBP at initial conditions, when both phenol and benzoic acid concentrations are the maximum, the selectivity would be highest. Indeed this is clearly reflected in Fig. 6.

### 3.8. Reusability of catalyst

The catalyst reusability was studied twice, including the use of fresh catalyst (Table 2). After each run, the catalyst was filtered, refluxed with 30 cm<sup>3</sup> methanol for 1 h, dried at 120 °C for 3 h, and weighed before using in the next batch of reaction. There was some attrition of catalyst particles during agitation. In a typical batch reaction, there was an inevitable loss of particles during filtration due to attrition. Since no make-up amount was added, based on unit mass of catalysts, the initial rates were nearly the same, thereby suggesting excellent catalyst stability. In order to validate these arguments, the catalyst after second reuse was treated as given earlier and a make-up quantity of fresh catalyst was added to get excellent reproducibility of the results which shows that the catalyst is active and stable.

### 3.9. Direct Fries rearrangement of phenyl benzoate

The direct Fries rearrangement of phenyl benzoate was studied at 200 °C in chlorobenzene as a solvent with a catalyst loading of 0.05 g/cm<sup>3</sup> (Fig. 7). A conversion of 60% of phenyl benzoate was obtained after 3 h. The selectivity for 4-hydroxybenzophenone and 2-hydroxybenzophenone were 12% and 4%, respectively. Phenol and benzoic acids were obtained as major by-products. This would suggest a reverse reaction is still predominant as shown in Scheme 1. Thus direct acylation by routes 2 and 3 contributes substantially in comparison with Fries rearrangement. Thus, the single pot synthesis of the formation of 4-hydroxybenzophenone from phenol and benzoic acid is much better.

## 4. Conclusion

The esterification reaction of phenol with benzoic acid, followed by the Fries rearrangement towards hydroxybenzophenones in a one-pot liquid phase operation was examined with several catalysts under solvent-free conditions. Novel nanocatalyst Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> supported on K-10 clay (designated as Cs-DTP/K-10) provided excellent activity and selectivity for the desired product. The selectivities of 2-hydroxybenzophenone and 4-hydroxybenzophenone were mainly dependant on the duration, temperature, phenol to benzoic acid mole ratio and catalyst loading. The esterification was faster than the Fries rearrangement and was the main pathway in a two-step route and there is a direct acylation leading to the formation of 2- and 4-hydroxybenzophenones. The selectivity of 4-hydroxybenzophenone increases with temperature. The catalyst is active, stable, and reusable.

## Acknowledgements

GDY acknowledges support from the Darbari Seth Professor endowment and GG is grateful to the Ambuja Educational Institute, a Trust of M/s Gujarat Ambuja Cements Ltd, for bestowing

financial assistance as JRF. GDY acknowledges hospitality of Purdue University, West Lafayette as distinguished visitor under their Asia Initiative program.

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