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

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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 $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/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 $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 (most active) ~ (almost equal)UDCaT-5 > 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/HMS > 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^3 $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/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.

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 $AlCl_3$, $FeCl_3$, and Bronsted acids such as HF, H_2SO_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 absorbents 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 > $AlCl_3$ > H-mordenite ≈ H-ZSM-5 (minimum). H-beta showed the

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Nomenclature

a_P	solid–liquid interfacial area (cm^2/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 (mol/cm^3)
C_{A0}	initial concentration of A at solid (catalyst) surface (mol/cm^3)
C_B	concentration of B (mol/cm^3)
C_{B0}	initial concentration of B in bulk liquid phase (mol/cm^3)
C_{WP}	Wiesz–Prater parameter
D_{AB}	diffusion coefficient of A in B (cm^2/s)
D_{BA}	diffusion coefficient of B in A (cm^2/s)
D_e	effective diffusivity of benzoic acid (cm^2/s)
E_i	activation energy of ith 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_{obs}	overall rate of reaction based on liquid phase volume ($mol\,cm^{-3}\,s^{-1}$)
$r_{2\text{-HBP}}$	net rate of formation of 2-hydroxybenzophenone
$r_{4\text{-HBP}}$	net rate of formation of 4-hydroxybenzophenone
r_{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

Greek letters

ε	catalyst porosity
τ	tortuosity
ρ_p	density of catalyst particle (g/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 $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/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 (1.671×10^{-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 (6.688×10^{-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 preformed 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 ($ZrOCl_2{\cdot}8H_2O$) 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 $AgNO_3$ test. A material balance on chloride ions before and after precipitation and washing shows no retention of Cl^- on the solid. Zirconium hydroxide was dried in an oven for 24 h at 100 °C and was crushed to 100 mesh size. $Zr(OH)_4$ was then added to a solution containing 15 cm^3/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 $AgNO_3$ 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 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].