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Kinetics of Friedel–Crafts benzoylation of veratrole with benzoic anhydride using $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 solid acid catalyst

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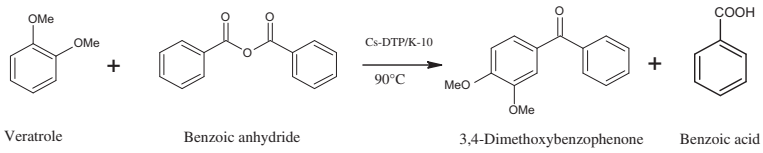
HIGHLIGHTS

- Solvent free benzoylation of veratrole with benzoic anhydride was carried out.
- $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 was the best and robust solid acid catalyst.
- Various reaction parameters affecting rate were studied.
- Kinetic model was developed using Eley–Rideal mechanism.
- Experimental and theoretical model fit the data well.

GRAPHICAL ABSTRACT



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ABSTRACT

Friedel–Crafts alkylation and acylation reactions are ubiquitous in several industries and use highly polluting liquid acids as catalysts. Production of ketones and subsequently secondary alcohols is achieved by Friedel Crafts acylation using various acylating agents. Benzophenone and its family are used in intermediates, fine chemicals, dyes and pharmaceuticals industries. Use of homogeneous catalysts in benzoylation of veratrole (1,2-dimethoxybenzene) to produce 3,4-dimethoxybenzophenone (DMBP) is highly polluting. The current work deals with solvent free reaction of veratrole and benzoic anhydride to produce 3,4-DMBP by using different solid super acids such as 20% (w/w) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 clay (Cs-DTP/K-10), UDCaT-5, sulfated zirconia (S-ZrO_2), unsupported Cs-DTP and montmorillonite K-10 clay. Cs-DTP/K-10 was found to be best catalyst for this reaction. At a mole ratio of 1:5 of benzoic anhydride to veratrole, the solvent free reaction gave 89.3% conversion at 90 °C in 2 h at catalyst loading of 4% (w/v). The selectivity was 100%. The catalyst is robust and reusable. It was characterized before and after use to find its fidelity. The effect of different parameters on the rate of reaction and conversion of veratrole was studied systematically to deduce kinetics of the benzoylation reaction. The reaction follows Eley–Rideal mechanism with weak adsorption of benzoic anhydride. The apparent energy of activation is 20.8 kcal/mol.

1. Introduction

Friedel–Crafts alkylation and acylation reactions are omnipresent in several industries and are traditionally catalyzed by highly polluting liquid acids. These reactions are mainly used in the synthesis of intermediates, insecticides, pharmaceuticals, agrochemicals, dyestuff, perfumes, flavors and fine chemicals [1,2]. Production of ketones and subsequently secondary alcohols is achieved by Friedel–Crafts acylation using a variety of acylating agents such as acid anhydrides, acid chlorides and carboxylic acids. Benzophenone and its substituted analogues are used in the fragrance and flavor industries and particularly anisole and dimethoxybenzenes can be acylated/benzoylated to make a variety of products [3,4]. Friedel–Crafts acylation is conducted using

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Nomenclature

A	reactant species A, veratrole
B	reactant species B, benzoic anhydride
AS	chemisorbed A
BS	chemisorbed B
C	3,4-dimethoxybenzophneone
D	benzoic acid
a_p	surface area per unit liquid volume (cm^2/cm^3)
A_0	concentration of A in bulk liquid phase (mol/cm^3)
B_0	concentration of B in bulk liquid phase (mol/cm^3)
C_A	concentration of A (mol/cm^3)
C_{AS}	concentration of A at solid (catalyst) surface (mol/cm^3)
C_B	concentration of B (mol/cm^3)
C_{BS}	concentration of B at solid (catalyst) surface (mol/cm^3)
C_C	concentration of C in (mol/cm^3)
C_D	concentration of D in (mol/cm^3)
C_S	concentration of vacant sites (mol/cm^3)
C_t	total concentration of the sites (mol/cm^3)
C_{wp}	Weisz Prater parameter
d_p	diameter of catalyst particle (cm)
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 (cm^2/s)
$k_{SL\text{-}A}$, $k_{SL\text{-}B}$	solid–liquid mass transfer coefficients (cm/s)
k_B	chemisorption rate constant for forward reaction
k'_B	chemisorption rate constant for backward reaction
k_{SR}	reaction rate constant ($cm^6\ mol^{-1}\ g^{-1}\ s^{-1}$)
K_B	adsorption equilibrium constant for B (cm^3/mol)
M	mole ratio of A to B
$-r_A$	rate of surface reaction of A ($mol\ cm^{-3}\ s^{-1}$)
$-r_B$	rate of chemisorption of B ($mol\ cm^{-3}\ s^{-1}$)
r_{obs}	observed rate of reaction based on liquid phase volume ($mol\ cm^{-3}\ s^{-1}$)
R_P	particle radius (cm)
s	vacant site
Sh	Sherwood number
w	catalyst loading (g/cm^3)
X_B	fractional conversion of B

Greek letters

ρ_p	density of catalyst particle (g/cm^3)
μ	viscosity of solvent (poise)
η	effectiveness factor
ε	porosity
τ	tortuosity

Acronyms

UDCaT-5	University Department of Chemical Technology catalyst-5
K-10	Montmorillonite clay
Cs-DTP/K10	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported on montmorillonite acid treated clay K-10

homogeneous catalysts such as $ZnCl_2$, $AlCl_3$, $FeCl_3$, $SnCl_3$, and $TiCl_4$ (Lewis acids), H_2SO_4 and HF (Bronsted acids) [4,5]. The Lewis acid catalysts are highly reactive and moisture sensitive leading to storage and transportation problems. Acylation reaction suffers from the deactivation of catalyst due to the formation of complex between the product and metal halide and hence, more than stoichiometric amount of catalyst is required [5,6]. The reaction is followed by neutralization of the complex which results in loss of catalyst and generation of huge corrosive waste stream requiring further treatment. Therefore, development of cleaner and benign catalytic technologies is necessary to minimize aqueous waste and reduce effluent treatment costs. Compared to the conventional homogeneous acids, heterogeneous catalysts have several merits such as use of different multi-phasic reactors and ease of their operation, simplicity of separation, reusability of catalyst and non-corrosive environment. Use of solid acid catalyst with acid anhydride as acylating agent offers a green option since the catalyst-product complex formation and its neutralization are totally avoided.

Benzoylation of veratrole (1,2-dimethoxybenzene) is industrially very important [7] and the ketone so produced can be further hydrogenated to get secondary alcohol which is commercially useful. A large body of literature has been published on solid acid catalyzed Friedel–Crafts acylation reactions of aromatic ethers using zeolites [8–10], sulfated zirconia and its modified forms [11–17], metal oxide supported acids such as UDCaT-5 [18], acidic clays [19,20], heteropolyacids (HPA) supported on clays [21–28], Nafion [29,30], hexagonal mesoporous silica [31,32], and carbon [33].

Heteropoly acid, especially dodecatungstophosphoric acid (DTP) having Keggin structure shows the highest Bronsted acidity and activity for Friedel–Crafts alkylation and acylation reaction [34–39]. Several problems associated with bulk HPA's such as very low surface area, high solubility in polar solvent, poor thermal stability and rapid deactivation can be overcome by the use of proper supports such as metal oxides, mesoporous material, alumina, active carbon, K-10 and/or by partial replacement of HPA's proton with metal ions such as Na^+, Al^{3+}, Cs^+, Ag^+, Fe^{3+}, Bi^{3+}, Ru^{3+}, Al^{3+}, Sm^{3+}, Ti^{4+}, Hf^{4+} [36]. Cs^+ substituted DTP has been reported to be more active and possesses high acidity as compared to the parental heteropoly acid [21]. We reported the novel step of supporting HPAs on the acid treated clay which results in enhancement in activity of catalyst as compared to parental HPAs. Similarly we synthesized the Cs-modified dodecatungstophosphoric acid (DTP) immobilized on acidic montmorillonite K-10 clay wherein the Keggin structure was intact and used as highly selective and active catalyst for several important industrial process [27,28,37,38].

Benzoylation of veratrole with benzoic anhydride over H-forms of various zeolites using chlorobenzene as a solvent was studied at 130 °C to get 75% conversion of veratrole in 60 min [8]. Liquid phase benzoylation of veratrole in solvent free condition was investigated on 15% silicotungestic acid on zirconia calcined at 750 °C as a catalyst, which gives 99% benzoic anhydride conversion at 120 °C in 120 min [7]. 20% (w/w) Cs-DTP/K-10 activity was compared with different catalysts for benzoylation of anisole with benzoyl chloride and found to be more active for the reaction [21]. However, the use of benzoyl chloride as a benzoylating agent results in the HCl generation which may results in reactor corrosion and environmental pollution. Zeolites usually suffer from reusability problems, while zirconium oxide's basic nature decomposes HPAs and leads to deformation of the parent Keggin structure [2]. A very few articles are available in the literature on the benzoylation of aromatic ethers using benzoic anhydride. Also there is no published detail on the kinetics of benzoylation of veratrole.

The present work deals with the preparation of active and reusable catalyst 20% (w/w) Cs-DTP/K-10 for benzoylation of veratrole using benzoic anhydride and development of a suitable kinetic model. The catalyst activity was compared with the reported literature. The fresh and spent catalyst was characterized fully to understand reaction mechanism and its reusability.