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Selective acylation of 1,3-dibenzyloxybenzene to 3,5-dibenzyloxyacetophenone over cesium modified dodecatungstophosphoric acid (DTP) on clay

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ABSTRACT

The Friedel-Crafts of acylation of aromatic ethers in liquid phase using solid acids is quite challenging, due to problems of deactivation. The ubiquitously used zeolites have several limitations since bulky aromatic ethers are known to deactivate them rapidly. Acylated aromatic ethers are used in a variety of industries such as pharmaceuticals and fine chemicals, perfumes and agrochemicals. In the current work, 1,3-dibenzyloxybenzene was acylated with acetic anhydride using several solid superacids to get 3,5-dibenzyloxyacetophenone, which is a very important precursor for the production of drugs for treatment of various diseases and disorders. The activities of 20% (w/w) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 clay, sulfated zirconia, UDCaT-5, Amberlyst-36 and Indion-130 were studied. 20% (w/w) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 clay was the most selective. A systematic study was undertaken to understand the reaction mechanism and catalyst functioning with $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10. The catalyst gets deactivated slowly over repeated use and this was studied independently. The adsorption of reactants and products was studied from pure component solutions and mixtures. The experimental data so generated were used to develop a model, incorporating deactivation. The model fits the experimental data very well. Further insight is provided using the model to avoid deactivation by proper selection of process parameters to get 100% selectivity.

1. Introduction

Friedel-Crafts acylation and alkylation reactions, catalyzed by acids, have been investigated extensively for the preparation of several useful products and precursors, which are commercially relevant in various industries such as fine chemicals and pharmaceuticals, agrochemicals, perfume and flavors. Friedel-Crafts acylation of an aromatic compound leads to ketones and the acylating agent is typically an acyl halide, acid anhydride, acid or ester. The catalyst forms an acylium ion intermediate from the interaction of acylating agent with acid. The conventional acid catalysts are homogeneous such as Lewis acids ($AlCl_3$, $FeCl_3$, $ZnCl_2$, $TiCl_4$, $ZrCl_4$) and Brønsted acids (polyphosphoric acids, HF) [1,2]. Homogeneous acid catalysts pose several problems, such as difficulty in separation and recovery, contamination of the product with impurities resulting from the acid, disposal of the spent catalyst, corrosion of equipment and high toxicity. The homogeneous acids are employed in more than stoichiometric quantities over the substrate to be acylated; and they cause severe corrosion of the reactor and auxiliary equipment and also form byproducts. The acylating agents used in most of the traditional processes are the expensive and polluting acyl halides that require special care in handling and workup. Development of reusable solid-acid catalysts having high activity for liquid phase Friedel-Crafts type of acylation reactions is, therefore, of great importance. In view of the increasingly strict environmental legislations, considerable efforts have been directed to develop cleaner and greener Friedel-Crafts chemistry by using solid-acid catalysts which include zeolites, clays, heteropoly acids (HPA), sulfated zirconia and titania, ion exchange resins, etc. [3–6]. Solid-acid catalysts are easy to recover and reuse, produce no salts, overcome corrosion problems, thereby allowing use of cheaper materials of construction.

Notwithstanding the above advantages, acylations of substituted aromatics, particularly ethers, with solid-acid catalysts are quite challenging. The ubiquitously used zeolites have several limitations since aromatic ethers are known to deactivate them; for instance, zeolites are deactivated rapidly with aromatic ethers such as anisole and veratrole [7,8]. Heteropoly acids supported on hexagonal mesoporous silica (HMS) are quite robust catalysts for acylation [9], whereas ion exchange resins were found to deactivate in acylation of diphenyl oxide and thioanisole [10,11].

There is no report in the published literature on the acylation of 1,3-dibenzyloxybenzene using heterogeneous catalyst including

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Nomenclature

a_p	catalyst particle surface area per unit liquid volume (cm^2/cm^3)
A	1,3-dibenzyloxybenzene
$[A_0]$	initial concentration of 1,3-dibenzyloxybenzene (mol/cm^3)
$[A_S]$	concentration of 1,3-dibenzyloxybenzene at the external surface of the catalyst (mol/cm^3)
B	acetic anhydride
$[B_0]$	initial concentration of acetic anhydride (mol/cm^3)
$[B_S]$	concentration of acetic anhydride at the external surface of the catalyst (mol/cm^3)
C	acetic acid
C_A	concentration of A in the liquid phase (mol/cm^3)
C_{AL}	concentration of species A in the liquid phase at any time t (mol/cm^3)
C_{ALf}	final concentration of species A in the liquid phase at infinite time
$C_{I_{in}}$	initial concentration of Ith species (mol/cm^3)
$C_{I_{fin}}$	final concentration of Ith species (mol/cm^3)
d_P	particle diameter (cm)
D_e	effective diffusivity (cm^2/s)
I	Ith species
k_{DE}	deactivation rate constant
k_{SR}	forward reaction rate constant for surface reaction between A and B (cm^6 s/mol s g-cat)
K_{D1}, K_{D2}	desorption equilibrium constant for M and C, respectively
K_{M1}	adsorption equilibrium constant for M ($=1/K_{D1}$)
K_{C2}	adsorption equilibrium constant for C ($=1/K_{D2}$)
M	3,5-dibenzyloxyacetophenone
M_R	initial molar ratio of concentration of B to that of A
$-r_A$, $-r_B$	rate of reaction of A, B (mol/cm^3 s)
r_{obs}	observed rate of reaction (mol/cm^3 s)
S	vacant site
w	catalyst loading per unit volume of liquid phase (g/cm^3)
X_A	fractional conversion of A
ρ	density of particle (g/cm^3)

kinetic modeling. Thus the current work was undertaken. The product 3,5-dibenzyloxyacetophenone is widely used as intermediate in the production of a pharmaceutical for treatment of obesity, diabetes, glaucoma [12], AIDS, HIV infection [13], antiinflammatory effects [14], and also in the treatment of disorders which result from leukotriene**,** tranquilizers, hypotensives, diuretics, and antiglaucoma agents [15,16].

Heteropoly acids with the Keggin structure are good catalysts and among them dodecatungstophosphoric acid (DTP) which possesses the highest Brønsted acidity has been used in different forms. However, their low surface area, rapid deactivation, and relatively poor stability are some of the major problems associated with HPAs as catalysts in the bulk form [17]. The novelties of synergism between HPAs and acid-treated clays were brought out for the first time in our laboratory [18,19] including other systems of industrial relevance [19–26]. The clay-supported catalysts have lower surface areas in the range of 130–170 $m^2\ g^{-1}$, depending on the amount of loading, in comparison with 230 $m^2\ g^{-1}$ of K-10 clay. The surface area can be increased by using supports such as mesoporous silica [9,27], mesoporous aluminosilicates [28], alumina and carbon [29], and zirconia [30] and partial substitution of protons of HPAs with Cs^+ converts them to materials with higher surface area and improved thermal stability [17]. However, because of their basic nature alumina and zirconia decompose HPAs resulting in the deformation of the parent Keggin structure and causing a reduction in the overall activity [30]. Supporting HPA on a commercial montmorillonite clay such as K-10 overcomes this problem [18,19]. A novel method of supporting Cs-modified dodecatungstophosphoric acid, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, designated as Cs-DTP/K-10, was developed by us [31].

Cs-DTP retains the Keggin anion intact and results in a very active and selective catalyst useful in a variety of industrially important reactions [32–36] and regioselective separations [36].

The current work deals with process development and kinetic aspects of acylation of 1,3-dibenzyloxybenzene with acetic anhydride to 3,5-dibenzyloxyacetophenone by using a variety of solid-acid catalysts. The studies also include dynamic adsorption experiments, modeling of deactivation and methods to overcome such problems. Scheme 1 shows the monoacylated product and there was a subsequent diacylation in the benzyloxy ring. There is a steric hindrance in the main ring and thus the acyl group goes in to the side ring. Therefore to improve the selectivity the effects of various parameters were studied.

2. Experimental

2.1. Chemicals and catalysts

All chemicals and catalysts were procured from firms of repute and used without further purification as follows:

Acetic anhydride (AR grade; s. d. Fine Chem. Ltd., India), K-10 clay (Aldrich, USA), ion exchange resins Indion-130 (Ion Exchange (India) Ltd.) Amberlyst-36 (Rohm and Hass, USA).

All resins were available in, or converted to, H^+ form by standard methods and dried at 120 °C before use. Heteropoly acids were obtained from M/s. s. d. Fine Chemicals Pvt. Ltd. The following catalysts were synthesized in the laboratory by established procedures: 20% (w/w) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 [31], sulfated zirconia [4] and UDCaT-5 [37]. 1,3-Dibenzyloxybenzene was prepared and purified in the laboratory as per a reported procedure [38]. 3,5-Dibenzyoxyacetophenone of pure grade was obtained as gift sample from M/s Amrutanjan Fine Chemicals Ltd., Chennai, India.

2.2. Reaction procedure

The reaction was carried out in a 100 ml capacity glass reactor of 5 cm internal diameter and it was equipped with four equally spaced baffles and a standard six-blade pitched turbine impeller, and a reflux condenser. The reaction temperature was maintained by means of a thermostatic oil bath in which the reaction assembly was immersed. The standard experiments were carried out with 0.02 mol 1,3-dibenzyloxybenzene and 0.06 mol acetic anhydride and the volume was made up to 30 ml with chlorobenzene as a solvent at a temperature of 80 °C. The catalyst loading was 0.1 g/cm^3. The reaction mixture was allowed to reach the desired temperature and the initial/zero time sample collected. Agitation was then commenced at a known speed which was 1000 rpm for all experiments except where the effect of speed was studied. Samples were withdrawn periodically and analyzed by GC (gas chromatography). At the end, the catalyst was separated by filtration and the products were confirmed by GC–MS.