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Ion-Exchange Resin Catalysis in Benign Synthesis of Perfumery Grade *p*-Cresylphenyl Acetate from *p*-Cresol and Phenylacetic Acid

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Abstract:
***p*-Cresylphenyl acetate is a very important perfume that finds wide applications and possesses an organoleptic character similar to those of honey, nuts, and butter. It is produced by mineral acid-catalyzed esterification of *p*-cresol with phenylacetic acid. Use of homogeneous acid catalysts leads to posttreatment pollution problems apart from the quality-related issues. The current work is focused with an eco-friendly and benign catalytic process, employing the solid acid catalysts such as dodecatungstophosphoric acid (DTP) supported on K-10 clay, ion-exchange resins, sulfated zirconia, etc. for esterification of *p*-cresol with phenylacetic acid to *p*-cresylphenyl acetate. The order of catalytic activity was found to be Amberlyst-15 ≈ Indion-125 > 20% w/w DTP/K-10 > sulfated zirconia. Indion-125 was used for further experiments. It was observed that the catalyst has excellent reusability and that the reaction was 100% selective towards *p*-cresylphenyl acetate. A pseudo-first-order kinetic model was built up to fit the experimental data, and the apparent activation energy was found to be 9.56 kcal/mol.**

1. Introduction

Esterification is one of the most fundamental and important reactions used by industry because of the overwhelming applications of esters as intermediates in the synthesis of fine chemicals, drugs, plasticizers, perfumes, food preservatives, cosmetics, pharmaceuticals, solvents, and chiral auxiliaries.[1−4] Production capacity for esters varies anywhere from a few kilograms to several thousand kilograms per day.[1−5] Several synthetic routes have been adopted to make esters,[1,4] but most of them do not meet the stringent specifications that are being applied in today's chemically conscious world. The most traditional method of making an ester is the mineral acid-catalyzed reaction of the concerned carboxylic acid with an alcohol, with one of them taken in molar excess to shift the equilibrium conversion favourably by using a homogeneous catalysts such as sulfuric acid, *p*-toluene sulphonic acid, HF, HCl, phosphoric acid, etc. The advantages of using solid heterogeneous catalysts are too well-known and among these are zeolites, clays, ion-exchange resins, supported heteropoly acids, etc.[6−17] The current work is concerned with the use of cation-exchange resins to develop an environmentally benign process for *p*-cresylphenyl acetate. The importance of ion-exchange resins as catalysts has been reported in several commercially relevant reactions in comparison with other catalysts in our laboratory.[18−33]

p-Cresylphenyl acetate imparts a warm, animal-like background when used in jasmine, narcissus, and jonquille compositions.[2,3] It is very useful as a fixative and is easier to use than many other *p*-cresol derivatives. It also finds wide application in fine fragrance, beauty care, soap, laundry care, household products and possesses an organoleptic character similar to those of honey, nuts, and butter. Among solid catalysts, ion-exchange resins have been used for relatively low-temperature reactions and are available in a variety of forms and strengths. Apart from their prominence in separation and purification of products, ion-exchange resins[4,11−13] have been used as catalysts in the manufacture of some important chemicals such as MTBE, TAME, bisphenol A, phenol alkylation, and dimethyl maleate; also the deactivation of ion-exchange resins has been studied and modeled for industrial alkylation and acylation reactions.[12−31]

In our laboratory, we have examined the efficacy of ion-exchange resins with the reference to other solid acid catalysts such as clays and their modified forms, supported

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heteropoly acids (HPA), zeolites, sulfated zirconia, a series of UDCaT catalysts for developing clean and green industrial processes in consonance with basic principles of green chemistry. In continuation of our concerted efforts in developing ecofriendly, active, and selective catalysts, especially for esterification reactions where water is formed as coproduct and has a significant impact on equilibrium and overall conversion, the current work was undertaken. Furthermore, there is practically no literature available on the kinetics of esterification of *p*-cresol with phenylacetic acid by using ion-exchange resin as catalysts. Hence, it would be of special interest to study the esterification of *p*-cresol with phenylacetic acid over cheap and easily available catalysts such as ion-exchange resins.

2. Experimental Section

2.1. Chemicals and Catalysts. Cation-exchange resins Indion-125 and Amberlyst-15 were obtained from M/s Ion Exchange (India) Ltd, Mumbai, India, and Rohm and Haas, U.S.A., respectively. K-10 clay was obtained from Fluka, Germany. Zirconium oxychloride, dodecatungstophosphoric acid, phenylacetic acid, *p*-cresol were obtained from M/s s.d. Fine Chemicals Pvt Ltd., Mumbai. All other chemicals were analytical grade reagents and were used without further purification. The catalysts used for the reaction were dried at 110 °C for 4 h before use. Dodecatungstophosphoric acid (DTP)/K-10 (20% (w/w)) was prepared by a well-established procedure in our laboratory.[31,32] Sulfated zirconia was also prepared by an established procedure in our laboratory.[33,34]

2.2. Experimental Procedure, Analysis, and Isolation of Product. All experimental studies were conducted in a glass reactor of 5 cm i.d. and 10 cm height with four glass baffles and four bladed disc turbine impellers located at a height of 0.5 cm from the bottom of the vessel and mechanically agitated with an electric motor. A typical experiment utilized 0.2 mol of *p*-cresol and 0.006 mol of phenylacetic acid with a catalyst loading of 0.025 g/cm^3 on dry basis of total reaction volume at a agitation speed of 1000 rpm at 90 °C under solventless conditions. The reaction mixture was allowed to reach the desired temperature, the initial/zero time samples were withdrawn, and catalyst was added thereafter. The analysis was done on a gas chromatograph (Chemito 8610) equipped with a flame ionisation detector. A stainless steel column (2.5 m in length) packed with 10% OV-17 supported on chromosorb-WHP was used for the analysis. The injector and detector were kept at 300 °C. The oven temperature was programmed from 130 °C (0.5 min) up to 280 °C with a ramp rate of 20 °C min^{-1}. Synthetic mixtures were used to calibrate and quantify the data. The product was confirmed by GC−MS.

An increase in mole ratio enhances the conversion by orders of magnitude and is 95% at a mole ratio of 1:30 of phenylacetic acid:*p*-cresol. The equilibrium is shifted greatly to the right. The reaction is done under solventless conditions. The reaction was conducted at 90 °C at which it was a clear liquid solution. The catalyst was removed by hot filtration, and then the mass was cooled to 50 °C or so, whereby the solid product was crystallized and filtered. The reaction mass containing the unreacted *p*-cresol, phenylacetic acid, and traces of product was recycled. There was no foreign impurity introduced in the system. The product was purified by recrystallization in methanol. Thus, product separation and recovery and recycle of unreacted *p*-cresol was facilitated under such reaction conditions. Moreover, the homogeneous process, with drawbacks such as safe handling and disposal of corrosive mineral acids, has been replaced with a better heterogeneous catalytic process.

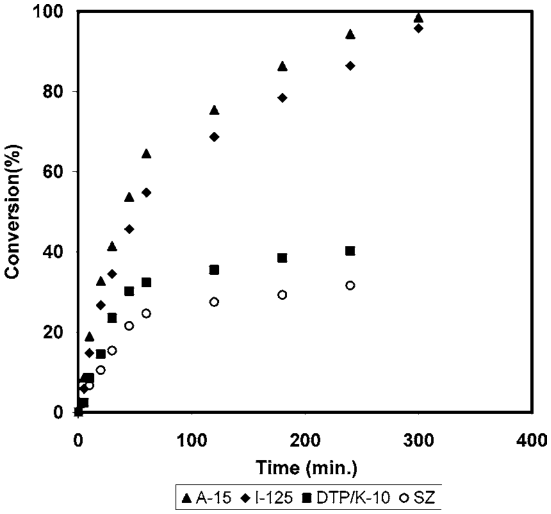
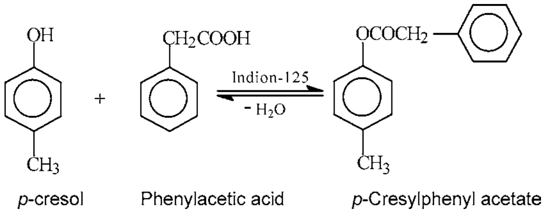


Figure 1. **Effect of various catalysts. *p*-Cresol; 0.2 mol; phenylacetic acid: 0.006 mol; speed of agitation: 1000 rpm; temperature: 90 °C.**

2.3. Reaction Scheme.



3. Results and Discussion

3.1. Effect of Various Catalysts. Different solid acid catalysts were used to assess their efficacy in this reaction. A 0.05 g/cm^3 loading of catalyst based on the organic volume of the reaction mixture was employed at a mole ratio of 30:1 *p*-cresol to phenylacetic acid at 90 °C and an agitational speed of 1000 rpm. The catalysts used were Amberlyst-15, Indion-125, 20% w/w DTP/K10, and sulfated zirconia. It was found that cation-exchange resins Amberlyst-15 and Indion-125 showed higher conversions compared to other catalysts. Figure 1 shows the conversion of phenylacetic acid, the limiting reactant, for the various catalysts. The esterification with ion-exchange resins Amberlyst-15 and Indion-125 was quantitative and almost equivalent since basically these have nearly similar exchange capacity. The ion-exchange capacities of Amberlyst-15 and Indion-125 are 4.90 and 4.86 mequiv/g-dry basis, respectively. There is only a slight difference (3%) which can be taken as experimental error. DTP/K10 (20% w/w) and S-ZrO_2 offered low conversion. It also suggests that Brønsted acids work better in esterifi-

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cation reactions. Further experiments were conducted with Indion-125 as the catalyst where only one parameter was varied at a time under otherwise similar experimental conditions. The selection of Indion-125 was also based on its availability in local market at much cheaper rates than the imported Amberlyst-15.

3.2. Effect of Speed of Agitation. This is typical solid−liquid slurry reaction involving transfer of *p*-cresol (A) and phenylacetic acid (B) from bulk liquid phase to catalyst surface wherein external mass transfer of reactants to surface of the catalyst particle, followed by intraparticle diffusion, adsorption, surface reactions, and desorption take place. To develop a true kinetic model the influence of the external solid−liquid mass transfer resistance must be ascertained.

The overall reaction can be presented as follows:

$$\mathrm{A} + \mathrm{ZB} \xrightarrow{\text{solid acid catalyst}} \mathrm{E} + \mathrm{W} \tag{1}$$

where A = phenylacetic acid, B = *p*-cresol E = *p*-cresylphenyl acetate, W = water and z = stoichiometric coefficient reaction which is 1 for the present cases.

At steady state, the rate of mass transfer per unit volume of the liquid phase (mol cm^{-3} s^{-1}) is given by:

$$R_{\mathrm{A}} = k_{\mathrm{SL-A}}a_{\mathrm{P}}\{[\mathrm{A_o}] - [\mathrm{A_s}]\} \tag{2}$$

(rate of transfer of A from bulk liquid to external surface of the catalyst particle)

$$= k_{\mathrm{SL-A}}a_{\mathrm{P}}\{[\mathrm{B_o}] - [\mathrm{B_s}]\} \tag{3}$$

(rate of transfer of B from bulk liquid to external surface of the catalyst particle)

$$= r_{\mathrm{obs}} \tag{4}$$

(observed rate of reaction within the catalyst particle)

Here the subscripts “o” and “s” denote the concentration in bulk liquid phase and external surface of the catalyst, respectively.

Depending on the relative magnitudes of external resistance to mass transfer and reaction rates, different controlling mechanisms have been put forward.[34] When the external mass transfer resistance is small, then the following inequality holds:

$$\frac{1}{r_{\mathrm{obs}}} \gg \frac{1}{K_{\mathrm{SL-A}}a_{\mathrm{P}}[\mathrm{A_o}]} \quad \text{and} \quad \frac{1}{K_{\mathrm{SL-A}}a_{\mathrm{P}}[\mathrm{A_o}]} \tag{5}$$

The observed rate could be given by three types of model wherein the contribution of intraparticle diffusion resistance could be accounted for by incorporation of the effectiveness factor η. These models are:

(1) the power law model if there is very weak adsorption of reactant species

(2) the Langmuir−Hinshelwood−Hougen−Watson model

(3) the Eley−Rideal model. It is there therefore necessary to study the effect of speed of agitation, catalyst loading, and particle size to ascertain the absence of external mass and intraparticle diffusion resistance so that the true intrinsic kinetic equation anc be used.

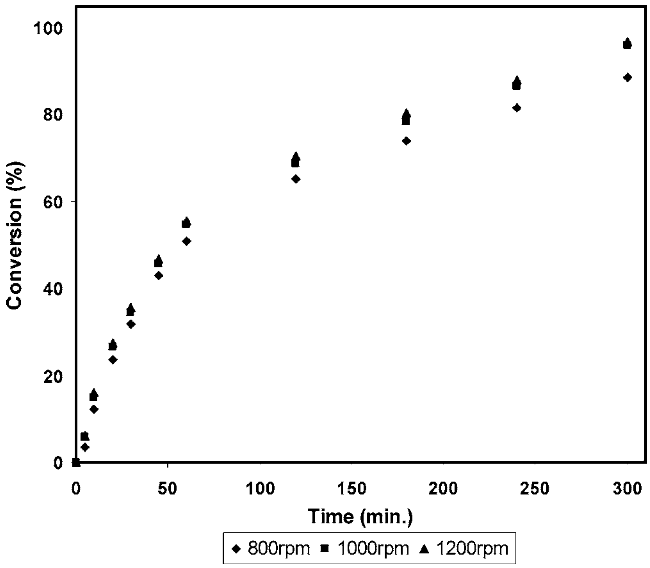

Figure 2. **Effect of speed of agitation. *p*-Cresol: 0.2 mol; phenylacetic acid: 0.006 mol; Indion-125: 0.05 g/cm^3. Particle size: 500−710 μm; temperature: 90 °C.**

In all reactions, *p*-cresol was taken in far molar excess (30:1) over phenylacetic acid to drive the equilibrium toward the ester. To establish the influence of external resistance to mass transfer of the reactants to the catalyst surface, the speed of agitation was varied over the range of 800−1200 rpm, for an average particle size of 500 μm. The conversion of phenylacetic acid, the limiting agent, at different intervals of time is shown in Figure 2. It was observed that the speed of agitation had no effect of conversion beyond 1000 rpm; thus, there was no limitation of external mass transfer of *p*-cresol from bulk liquid phase to the outer surface of the catalyst beyond this speed. Further experiments were conducted at 1000 rpm.

According to eq 5, it is necessary to calculate the rates of external mass transfer of both *p*-cresol (B) and phenylacetic acid (A) and compare them with the rate of reaction.

For typical spherical particle, the particle surface area per unit volume is given by

$$a_{\mathrm{P}} = \frac{6w}{(\rho_{\mathrm{P}}d_{\mathrm{P}})} \tag{6}$$

where w is the catalyst loading (g/cm^3) of liquid phase, ρ_{P} the density of particle (g/cm^3), and d_{P} is the particle diameter (cm). For this reaction, for the maximum catalyst loading used (0.1 g cm^{-3}) with a particle size (d_{P}) of 0.05 cm, in the current studies, a_{P} = 20 cm^2/cm^3 liquid phase.

For the maximum catalysts loading used in the current studies, a_{P} =20 cm^2/cm^3. The solid−liquid mass transfer coefficient, k_{SL}, for the two reactants was calculated by using the correlations of Sano et al.[35] which have been developed for ion-exchange resin-type catalysts and take into account the effects of Reynolds number and Schmidt number

$$\frac{k_{\mathrm{SL}}d_{\mathrm{P}}}{D\psi} = 2 + 0.4\left(\frac{e d_{\mathrm{P}}{}^{4}\rho_{\mathrm{L}}{}^{3}}{\mu_{\mathrm{L}}}\right)^{1/4}\left(\frac{\mu_{\mathrm{L}}}{\rho_{\mathrm{L}}D}\right)^{1/3} \tag{7}$$

where D is bulk diffusivity of the species (A or B), (in

cm^2s^{-1}), ψ is shape factor, μ_L = viscosity of liquid phase, ρ_L= liquid density (g cm^{-3}), e = power consumption in (ergs s^{-1}).

Where

$$e = \frac{P}{\rho_L V_L} = \text{energy supplied per unit mass of slurry by agitation, } cm^2/s^3 \tag{8}$$

where, the power is given by

$$P = NpN^3 D_I^{\,5} \rho_L \tag{9}$$

To evaluate N_P it is necessary to calculate the Reynolds number, which is given by

$$N_{Re} = \frac{D_I^{\,2} N \rho_L}{\mu_L} \tag{10}$$

N_P = power number, N = speed of agitation, rps, D_I = impeller diameter, cm, V_L = volume of the liquid phase, ρ_L = liquid density (g cm^{-3}).

The diffusivity values (D) can be calculated by using the Wilke−Change equation,[36] and these values are as follows: $D_{AB} = 4.77 \times 10^{-5}$ cm^2 s^{-1} and $D_{BA} = 4.86 \times 10^{-5}$ cm^2 s^{-1}. Thus, the corresponding values of the solid−liquid mass transfer coefficients for both of the reactants were obtained as follows: k_{SL-A} for phenylacetic acid is 2.79×10^{-3} cm/s for k_{SL-B} for p-cresol 2.84×10^{-3} cm/s. Thus, it was possible to calculate various resistances. A typical initial rate of reaction was calculated as 6.04×10^{-8} mol/cm^3·s, and therefore using appropriate values in eq 5, the following is obtained.

$$1.6 \text{ x } 10^7 \gg 1.9 \text{ x } 10^4 \quad \text{and} \quad 5.9 \text{ x } 10^4 \text{ cm}^3\text{·s/mol}$$

The above inequality implies that there is an absence of resistance due to the solid−liquid external mass transfer for both the species A and B and the rate may be either surface-reaction controlled or intraparticle-diffusion controlled. Therefore, the effect of catalyst loading and particle size was studied to ascertain the influence of intraparticle resistance.

3.3. Effect of Catalyst Loading. In the absence of mass transfer resistance, the rate of reaction is directly proportional to catalyst loading based on the entire volume of the liquid phase. The catalyst loading was varied over a range of 0.01−0.1 g cm^{-3} on the basis of the total volume of the reaction mixture. Figure 3 shows the effect of catalyst loading on the conversion of phenylacetic acid. It indicates that as the catalyst loading is increased, the conversion of phenylacetic acid increases which is due to proportional increase in the number of active sites. At higher catalyst loading the rate of mass transfer is excessively high and therefore there is no more increase in the rate.

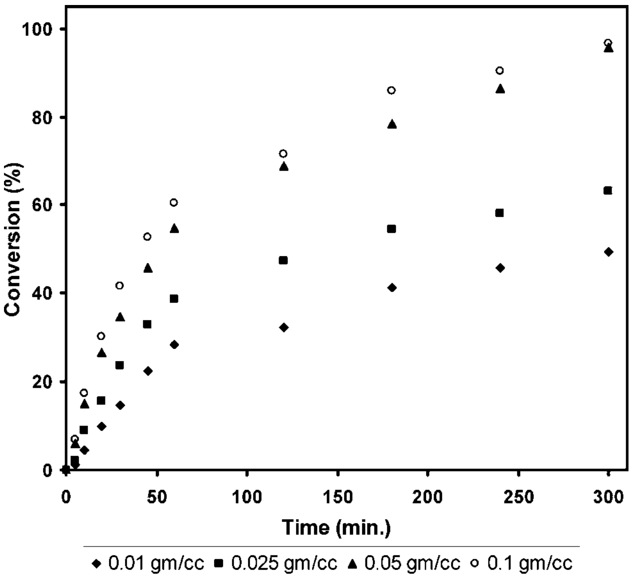

Figure 3. **Effect of catalyst loading. *p*-Cresol: 0.2 mol; phenylacetic acid: 0.006 mol; particle size: 500−710 *μ*m; speed of agitation: 1000 rpm; temperature: 90 °C.**

As shown by eqs 1 and 2, at steady state, the rate of external mass transfer to the exterior surface area of the catalyst is proportional to a_P, the exterior surface area of the catalyst where the concentrations of A and B are $[A_s]$ and $[B_s]$, respectively. For a spherical particle, a_P is also proportional to w, the catalyst loading per unit liquid volume as shown in eq 6. It is possible to calculate the values of $[A_s]$ and $[B_s]$; for instance,

$$k_{SL-A} a_P \{[A_o] - [A_s]\} = r_{obs}$$

at steady state.

$$\therefore \{[A_o] - [A_s]\} = 1.07 \times 10^{-6} \text{ mol/cm}^3$$

Thus, using the appropriate values, $[A_s] = 2.709 \times 10^{-4}$ mol cm^{-3} which is nearly equal to $[A_o]$ (2.72×10^{-4} mol cm^{-3}), similarly $[B_s] = [B]$. Thus, any further addition of catalyst did not have any bearing on external mass transfer. The experimental observation is thus consistent since the reaction could be limited by intraparticle diffusion or by reaction on the pore walls within the catalyst particle (intrinsic reaction), for which the effect of particle size needed to be considered.

3.4. Proof of Absence of Intraparticle Resistance. The effect of particle size of the catalyst on the reaction rate was studied by taking three different particle size ranges to assess the influence of intraparticle resistance. From Figure 4 it is observed that, as the particle size decreases, the conversion increases. However, the conversion for 710−500 and 300−200 μm differed only by a mere 2%. Thus, particles in the size range of 710−500 μm were used for further experiments. The average particle diameter of the catalyst used in the reactions was 0.06 cm, and thus, a theoretical calculation was done on the basis of the Wiesz−Prater criterion to assess the influence of intraparticle diffusion resistance.[37] According to the Wiesz−Prater criterion, the dimensionless parameter,

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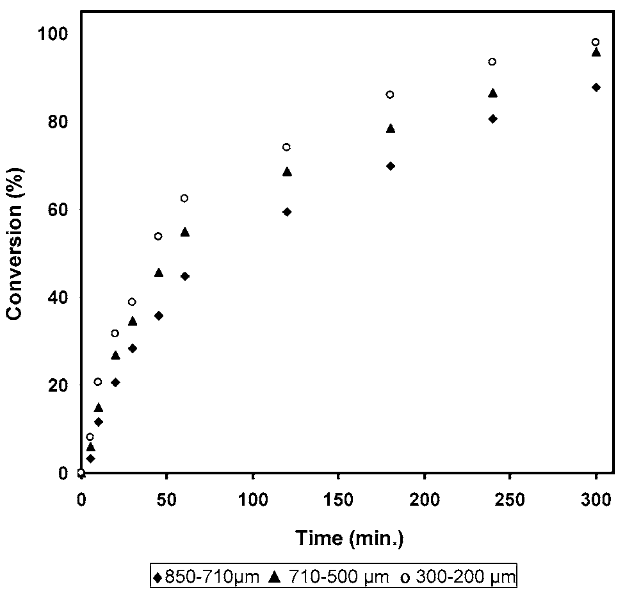

Figure 4. **Effect of particle size. *p*-Cresol: 0.2 mol; phenylacetic acid: 0.006 mol; Indion-125: 0.05 g/cm^3; speed of agitation: 1000 rpm; temperature: 90 °C.**

C_{wp}, which represents the ratio of the intrinsic reaction rate to intraparticle diffusion rate can be evaluated from the observed rate of reaction, the particle radius (R_P) and effective diffusivity of the limiting reactant (D_e), and the concentration of the reactant at the external surface of the particle.

$$\text{(i)}\quad \text{If}\quad C_{wp} = r_{obs}\rho_P R_P^2/D_e[A_s] \gg 1$$

then the reaction is limited by severe internal diffusion resistance.

$$\text{(ii)}\quad \text{If}\quad C_{wp} \ll 1$$

then the reaction is intrinsically kinetically controlled.

The effective diffusivity of phenylacetic acid (D_{e-A}) inside the pores of the catalyst was obtained from the bulk diffusivity (D_{AB}), porosity (ϵ), and tortusity (τ) as 9.7×10^{-6} cm^2 s^{-1} where $D_{e-A} = D_{AB}(\epsilon/\tau)$. In the present case, the value of C_{wp} was calculated as 4.3×10^{-2} for the initial observed rate which is much less than 1, and therefore, the reaction is intrinsically kinetically controlled. A further proof of the absence of the intraparticle diffusion resistance was obtained by studying the effect of temperature.

3.5. Effect of Mole Ratio. The mole ratio of phenylacetic acid to *p*-cresol was changed from 1:1 to 1:30 mol under otherwise similar sets of conditions. With an increase in mole ratio, the conversion of phenylacetic acid had increased (Figure 5).

3.6. Effect of Temperature. The effect of temperature on conversion under otherwise similar conditions was studied in the range of 70−100 °C as shown in Figure 6. The conversion of phenylacetic acid was found to increase substantially with increasing temperature up to 100 °C.

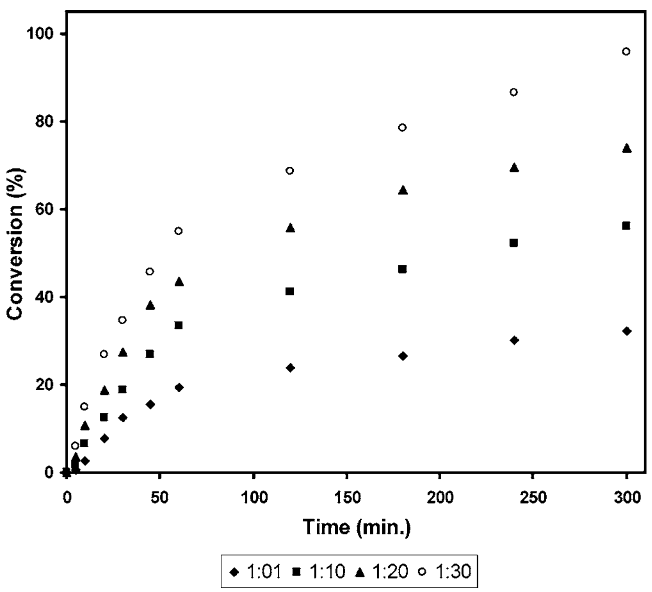

Figure 5. **Effect of mole ratio. Phenylacetic acid: *p*-cresol, Indion-125 0.05 g/cm^3. Particle size: 500−710 *μ*m; speed of agitation: 1000 rpm; temperature 90 °C.**

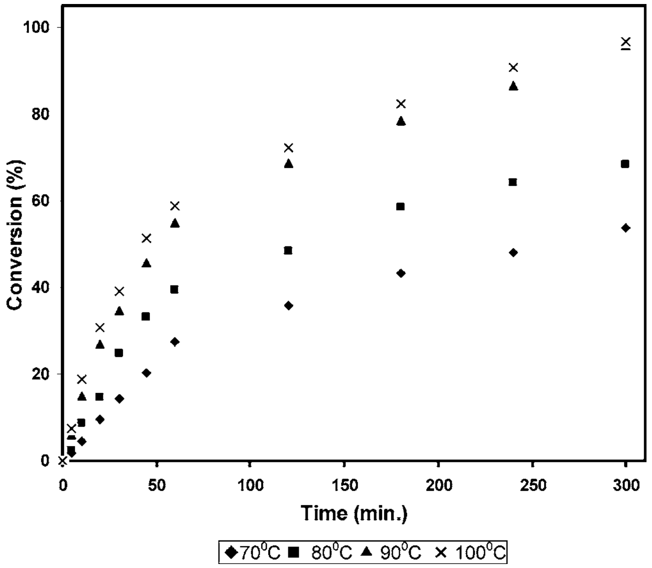

Figure 6. **Effect of temperature. *p*-Cresol: 0.2 mol; phenylacetic acid: 0.006 mol; Indion-125: 0.05 g/cm^3. Particle size: 500−710 *μ*m; speed of agitation: 1000 rpm; temperature: 90 °C.**

To elucidate the kinetic parameter a pseudo-first-order model was attempted with the experimental data (Figure 7), and it was found to fit the data well. The values of rate constants at different temperatures were calculated and an Arrhenius plot (Figure 8) was used to estimate the frequency factor and energy of activation. The values of the frequency factor k_0 and the energy of activation were calculated as 6×10^3 cm^3 mol^{-1} s^{-1} and 9.56 kcal/mol, respectively. This activation energy also supported the fact that the overall rate of reaction is not influenced by either external mass transfer or intraparticle diffusion resistance and it is an intrinsically kinetically controlled reaction on active sites.

3.7. Reusability of Catalyst. Reusability of Indion-125 was tested by conducting two runs (Figure 9). It is observed that for every reuse the rate of reaction and conversion decreases. After the reaction, the catalyst was filtered and then refluxed with 50 mL of toluene for 30 min to remove any adsorbed material from the catalyst surface and pores and dried at 110 °C after every use. It was observed that there is only a marginal decrease in conversion, in the final

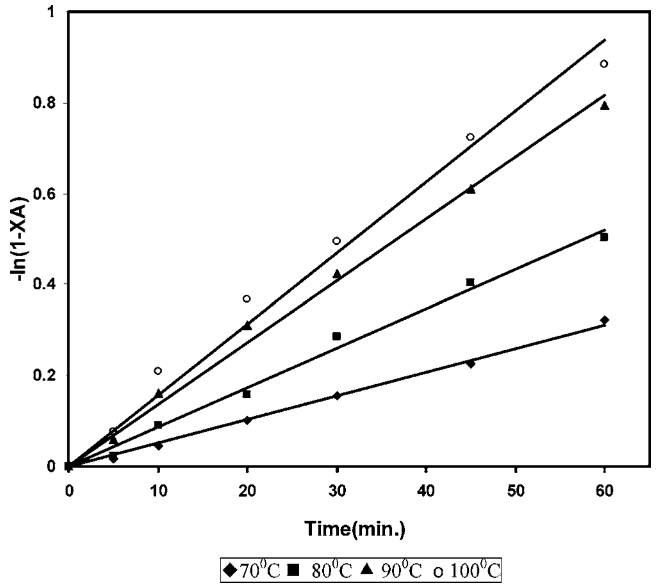

Figure 7. **Pseudo-first-order kinetic plot of esterification of *p*-cresol with phenylacetic acid.**

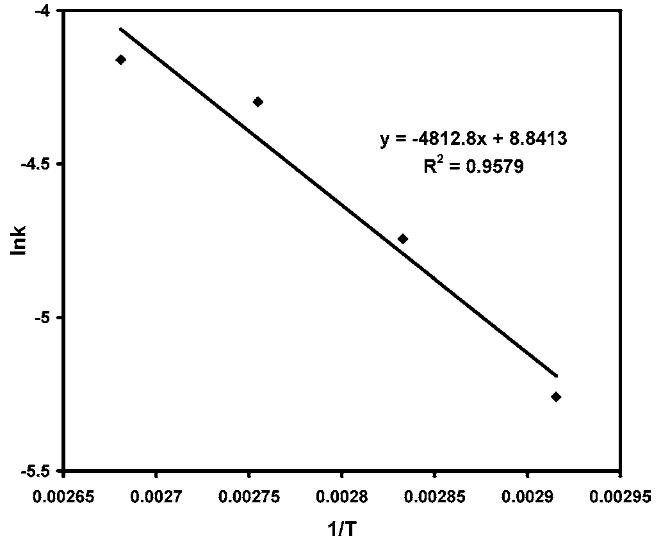

Figure 8. **Arrhenius plot.**

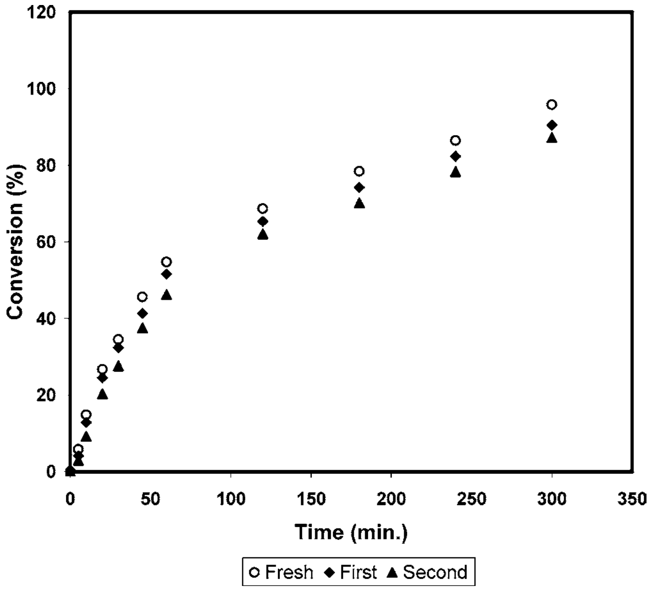

Figure 9. **Reusability of catalyst. *p*-cresol: 0.2 mol; phenylacetic acid: 0.006 mol; Indion-125: 0.05 g/cm^3. Particle size: 500−710 μm; speed of agitation: 1000 rpm; temperature: 90 °C.**

conversion from 95 to 87% in second reuse. Some catalyst was lost during filtration. There was no makeup catalyst added during the second use. Thus, the catalyst was reusable up to three times. The product is perfumery grade with no contamination of any mineral acid or sulfur.

4. Conclusions

The current work has focused on the synthesis of perfumery-grade *p*-cresyl-phenyl acetate by esterification of *p*-cresol with phenylacetic acid using different solid acid catalysts such as Amberlyst-15, Indion-125, 20% w/w DTP/K-10, and sulfated zirconia. The order of catalytic activity was found to be Amberlyst-15 > Indion-125 > DTP/K-10 > sulfated zirconia. Indion-125 was used for further experiments. It was observed that the catalyst has excellent reusability, and the reaction was 100% selective towards *p*-cresyl phenylacetate A pseudo-first-order kinetic model was built up to fit the experimental data, and the apparent activation energy is 9.56 kcal/mol, which also suggested that the reaction is intrinsically kinetically controlled. The product separation workup is simple.

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NOMENCLATURE

A = phenylacetic acid
[A_i] = concentration of phenylacetic acid at i, mol/cm^3
B = *p*-cresol
[B_i] = concentration of B at i, mol/cm^3
E = *p*-cresylphenyl acetate
H = water
Z = stoichiometric coefficient
a_P = solid−liquid interfacial area, cm^2/cm^3
D_{AB} = mutual diffusion coefficient of solute A at very low concentration in solvent B, cm^2/s
k_{SL-A}, k_{SL-B} = solid−liquid mass-transfer coefficients for A and B
D_e = effective diffusivity cm^2/s
d_P = diameter of the particle, cm

Greek Symbols

ρ_P = density of catalyst particle, g/cm^3
η = effectiveness factor
τ = tortuosity, dimensionless

Subscripts

o = bulk phase
s = catalyst surface

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