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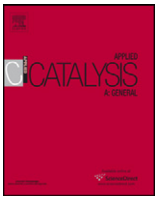

Friedel–Crafts propionylation of veratrole to 3,4-dimethoxypropiophenone over superacidic UDCaT-5 catalyst

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ABSTRACT

3,4-Dimethoxypropiophenone (3,4-DMPP) is of considerable commercial importance due to its use in fine chemical and drug industries. 3,4-DMPP is traditionally produced by the Friedel–Crafts propionylation of veratrole using homogeneous catalysts which are highly polluting. Zeolites have also been used but they are known to deactivate rapidly. A variety of novel solid acid catalysts such as UDCaT-4 (persulfated alumina zirconia on hexagonal mesoporous silica, HMS), UDCaT-5 (superacidic modified sulfated zirconia) and UDCaT-6 (modified sulfated zirconia nanoparticles on HMS) were synthesized in our laboratory and characterized. Amongst them UDCaT-5 was the most active and selective. The current work deals with development of clean and benign route for 3,4-DMPP synthesis using UDCaT-5 as catalyst in the absence of any solvent. Effects of various parameters were studied in order to optimize the conversion of veratrole and selectivity to 3,4-DMPP. Based on the experimental data a suitable mathematical model was developed to represent the reaction kinetics.

1. Introduction

Friedel–Crafts acylation and alkylation reactions are amongst the most versatile methods of synthesizing substituted aromatic compounds which serve as precursors for a variety of industrial processes [1]. Aromatic ketones are valuable intermediates as well as end products in an extensive range of value-added chemicals, which include pharmaceuticals, agrochemicals, biocides, flavors, fragrances and fine chemicals [2].

3,4-Dimethoxypropiophenone (3,4-DMPP) is of considerable commercial importance due to its use in fine chemical and drug industries. 3,4-DMPP is traditionally produced by the Friedel–Crafts propionylation of veratrole (VT) by using homogeneous catalysts such as $AlCl_3$, $TiCl_4$, $FeCl_3$, $SnCl_4$, CF_3SO_3H, FSO_3H and H_2SO_4 [3,4]. These catalysts are highly polluting and corrosive. More than stoichiometric quantities of the catalyst are used which are neutralized at the end of reaction leading to effluent treatment problems. Recently, the use of solid catalysts, such as Nafion-H [5], clays [6], heteropoly acids [7], $FeSO_4$, $Fe_2(SO_4)_3$ and metal oxides promoted by sulfate ions (SO_4^{2-}/Al_2O_3), SO_4^{2-}/ZrO_2, SO_4^{2-}/TiO_2), have been reported for the Friedel–Crafts of acylation of aromatics [7–9]. However, there is a limited literature on veratrole propionylation to 3,4-DMPP [10].

In particular, sulfated zirconia is the most powerful solid superacid which is used in a number of reactions of industrial utility [11–19]. All published literature shows that sulfated zirconia has been prepared with a maximum 4% w/w of sulfur with preservation of tetragonal phase which is responsible for its superacidic nature. Above this sulfur content, the tetragonal phase of zirconia is strongly affected and the superacidity reduced. It would be most advantageous to synthesize sulfated zirconia with sulfur content above 4% while retaining the tetragonal phase to attain high superacidity. A series of novel catalysts, named as UDCaTs, were thus prepared. These catalysts have been tested in a number of reactions in our laboratory [20–24]. Yadav and Murkute reported for the first time the preparation of sulfated zirconia with the highest sulfur content (9%), by using chlorosulfonic acid as a new source for sulfate ion [23]. This new catalyst was designated as UDCaT-5. The acronym, UDCaT stands for the University Department of Chemical Technology (UDCT) by which this institute was popularly known until recently.

The current work delineates novelties of UDCaT series of catalysts in Friedel–Crafts acylation of veratrole using propionic anhydride under solventless conditions. UDCaT-5 was found to be the most active, selective and robust catalyst. The overall process is green and clean. This work also deals with development of a kinetic model.

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Nomenclature

A	reactant species A, veratrole
B	reactant species B, propionic anhydride
A_0	concentration of A in bulk liquid phase (mol/cm^3)
B_0	concentration of B in bulk liquid phase (mol/cm^3)
A_S	chemisorbed A
B_S	chemisorbed B
C	3,4-dimethoxy propiophenone
D	propionic acid
a_P	surface area per unit liquid volume, cm^2/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)
M	mole ratio of B to A
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)
$k_{\text{SL-}A}$, $k_{\text{SL-}B}$	solid–liquid mass transfer coefficients (cm/s)
D_e	effective diffusivity (cm^2/s)
C_{WP}	Weisz Prater parameter
R_P	particle radius, cm
k_B	chemisorption rate constant for forward reaction
k'_B	chemisorption rate constant for backward reaction
$-r_B$	rate of chemisorption of B (mol cm^{-3} s^{-1})
$-r_A$	rate of surface reaction of A (mol cm^{-3} s^{-1})
k_{SR}	reaction rate constant (cm^6 mol^{-1} g^{-1} s^{-1})
K_B	adsorption equilibrium constant for B (cm^3/mol)
r_{obs}	observed rate of reaction based on liquid phase volume (mol cm^{-3} s^{-1})
S	vacant site
Sh	Sherwood number
w	catalyst loading (g cm^{-3}) of the liquid phase
X_A	fractional conversion of A

Greek letters

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

2. Experimental

2.1. Chemicals and catalysts

The following chemicals were procured from reputed firms and used without further purification: Veratrole, propionic anhydride, zirconium oxychloride, aqueous ammonia solution (s.d. Fine Chem. Ltd., Mumbai, India), hexadecyl amine, chlorosulfonic acid (Spectrochem. Ltd., Mumbai, India), tetraethyl orthosilicate (Fluka, Germany). Hexagonal mesoporous silica (HMS) was prepared by a procedure described elsewhere [25]. The catalysts were dried at 393 K for 3 h before use. UDCaT-4, UDCaT-5 and UDCaT-6 were prepared according to the procedures developed by us [20,23,24].

2.1.1. Preparation of UDCaT-4

A mixture of 2.39 g zirconium oxychloride and 0.11 g aluminum nitrate was dissolved in deionised water and added to 5 g of precalcined hexagonal mesoporous silica (HMS) by the incipient wetness technique. The solid material was dried in an oven at 110 °C for 3 h. The dried material was hydrolyzed with ammonia gas and washed with deionized water until a neutral filtrate was obtained. The absence of chloride ion in the filtrate was detected by the silver nitrate test. A material balance on chloride ions before and after precipitation, and washing showed no retention on the solid. The solid was then dried in an oven for 24 h at 110 °C. Persulfation was carried out by immersing the above solid material in 0.5 M aqueous solution of ammonium persulfate for 30 min. It was dried at 110 °C for 24 h and calcined at 650 °C for 3 h to get the active catalyst UDCaT-4 [20].

2.1.2. Preparation of UDCaT-5

UDCaT-5 was prepared by adding aqueous ammonia solution to zirconium oxychloride 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 chloride ion was detected by $AgNO_3$ test. Zirconium hydroxide was dried in an oven for 24 h at 100 °C and was crushed to 100 mesh size. It was then added to a solution containing 15 cm^3/g of 0.5 M chlorosulfonic acid in ethylene dichloride and mixed using 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. The temperature was raised slowly to 120 °C and maintained for 24 h. Thereafter it was calcined at 650 °C for 3 h to get the active catalyst UDCaT-5 [23].

2.1.3. Preparation of UDCaT-6

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 material was hydrolyzed with ammonia gas and washed with distilled water until no chloride ions were detected which was confirmed by the $AgNO_3$ 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 oven-dried to evaporate the solvent at 120 °C for 30 min. The sample was then kept in an oven at 120 °C for further 24 h and calcined thereafter at 650 °C for 3 h to get the active catalyst UDCaT-6 [24].

2.2. Reaction procedure

The reaction was carried out in a 50 mL capacity glass reactor of 3.5 cm i.d. equipped with four equally spaced baffles and a six-bladed turbine impeller. The reaction temperature was maintained within 0.5 °C of the set value by means of a thermostatic oil bath, in which the reaction assembly was immersed. Standard experiments were carried out by taking 0.04 mol veratrole, 0.2 mol propionic anhydride and 3% v/v of n-dodecane (internal standard), and 1.26 g catalyst loading (0.04 g/cm^3 liquid-phase) at 80 °C. The total liquid phase volume was 31.5 cm^3. All 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 collected. Agitation was then commenced at a desired speed. Catalyst-free samples were withdrawn periodically up to 2 h.

2.3. Method of analysis

Analysis of the reaction mixture was performed by GC (Chemito, model 8610) by using flame ionization detector and a stainless steel column (3.25 mm diameter and 4 m length) packed with a stationary phase of 10% OV-17 supported on chromosorb-WHP. Typically

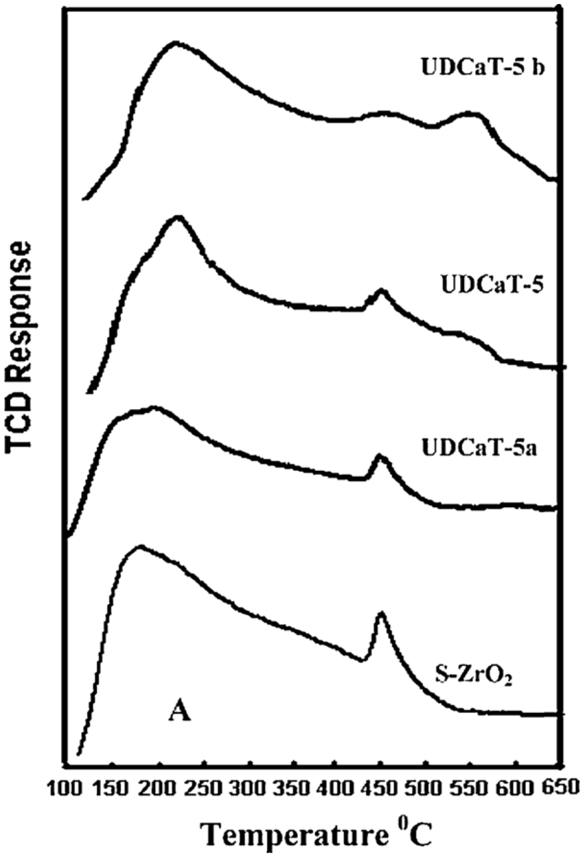


Fig. 1. Ammonia TPD: S–ZrO_2 and UDCaT-5 catalysts.

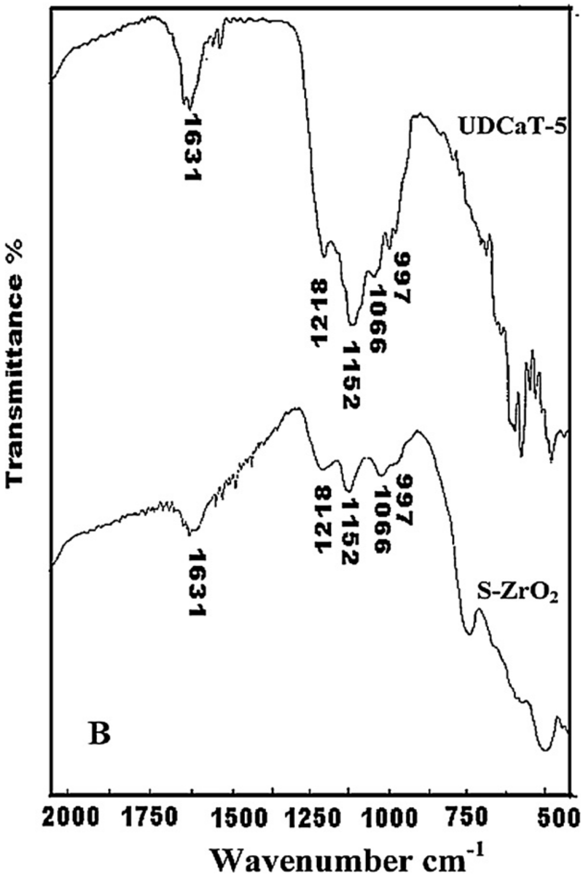


Fig. 2. FT-IR of S–ZrO_2 and UDCaT-5.

propionic anhydride was taken in excess and the conversions were based on the limiting reactant veratrole. The quantification of data was done through internal standard method. The products were confirmed by GC-MS.

3. Results and discussion

3.1. Characterization of UDCaT-5

UDCaT-5 was completely characterized by FT-IR, XRD, BET surface area, ammonia-TPD and elemental analysis and the details were published by our laboratory [23]. Only a few salient features are reported here. The ammonia-TPD was used to determine the acid strength of UDCaT-5. It shows that apart from intermediate and strong acidic sites present in sulfated zirconia, UDCaT-5 also contains superacidic sites (Fig. 1). The elemental analysis showed complete absence of chloride species and that 9% w/w S as sulfate was retained on the surface of UDCaT-5. In contrast, only 4% of S in the form of sulfate ion was retained on S–ZrO_2 wherein the sulfation was done by using 1N sulfuric acid. The FT-IR spectra of the S–ZrO_2 show a similar pattern as UDCaT-5 indicating the presence of bidentate chelating sulfate group (in C_{2v} symmetry with ν_3 at 1218, 1152, and 1066 and ν_1 at 997 cm^{-1}) coordinated to zirconia [26,27]. The absence of a band at 1400 cm^{-1} indicates that no polynuclear sulfates $S_2O_7{}^{2-}$ were formed on the surface of UDCaT-5. The band at 1631–1642 cm^{-1} is attributed to δ_{O-H}-bending frequency of water molecules associated with the sulfate group, suggesting that chlorosulfonic acid was decomposed during calcination at 923 K and the sulfate ions were retained on the surface of the UDCaT-5 (Fig. 2). Powder XRD was used to elucidate the crystalline phase of UDCaT-5 and S–ZrO_2 (Fig. 3). It is observed that crystal structure of zirconia is not affected by the high sulfur content of 9% in UDCaT-5 and the quantity of tetragonal phase of zirconia in UDCaT-5 is the same as that in the ordinary S–ZrO_2. The BET surface area of UDCaT-5 (83 $m^2\,g^{-1}$) is lower than that of S–ZrO_2 (103 $m^2\,g^{-1}$). The surface area of S–ZrO_2 gradually increases at low sulfate contents up to 4% w/w (119 $m^2\,g^{-1}$) but it decreases abruptly at a sulfate content of 5.64% (71 $m^2\,g^{-1}$) due to the migration of sulfate ions to the bulk phase of zirconia.

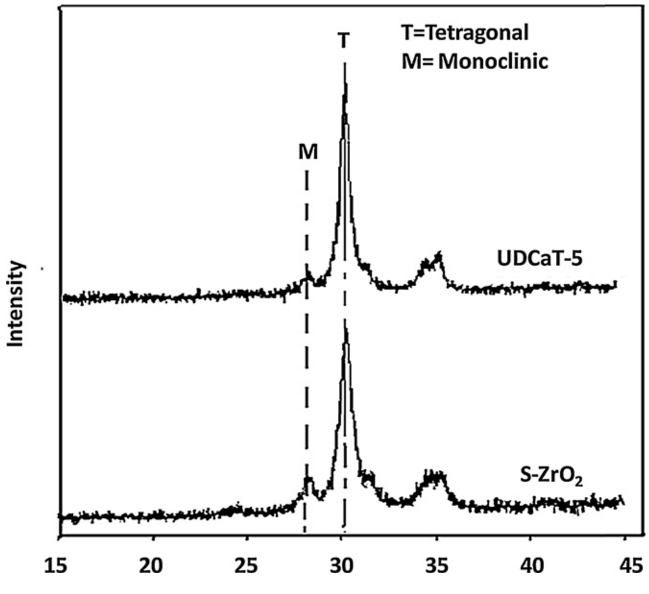


Fig. 3. XRD diffractogram S–ZrO_2 and UDCaT-5 catalyst.

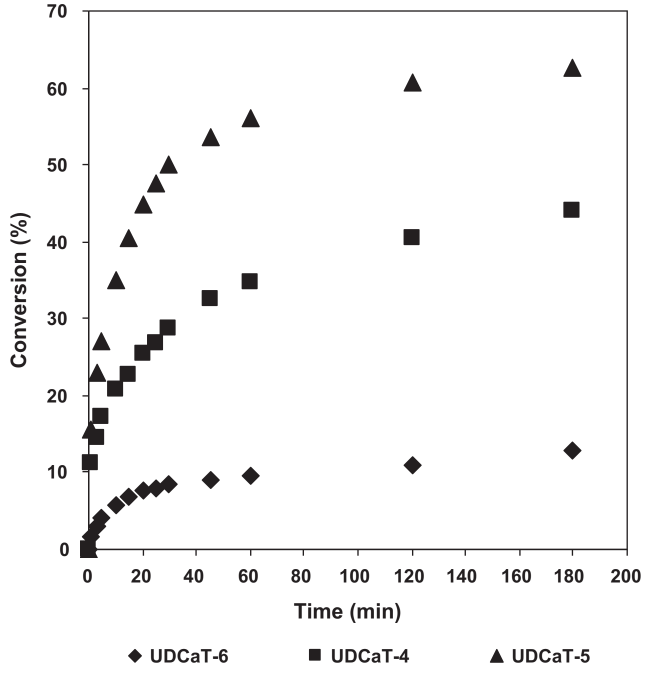


Fig. 4. Effect of various catalysts on conversion of veratrole. Veratrole: 0.04 mol, propionic anhydride: 0.2 mol, catalyst loading: 0.04 g/cm^3, temperature: 80 °C, speed of agitation: 1000 rpm.

3.2. Efficacies of various catalysts

Various solid acid catalysts based on sulfated zirconia were used to assess their efficacy in this reaction, namely, UDCaT-4 (persulfated alumina zirconia on HMS), UDCaT-5 (superacidic modified sulfated zirconia) and UDCaT-6 (modified sulfated zirconia nanoparticles on HMS). A 0.04 g/cm^3 loading of the particular catalyst based on the total organic volume of the liquid phase was employed at 80 °C at a speed of agitation of 1000 rpm. It was observed that UDCaT-4 and UDCaT-6 catalysts showed much lower conversions than UDCaT-5, although all of them are highly selective for 3,4-DMPP.

UDCaT-5 (most active) > UDCaT-4 > UDCaT-6 (least)

This is directly correlated with their acid strength. UDCaT-5 showed the highest activity (Fig. 4). Hence further experiments were conducted with UDCaT-5 due to its excellent activity and selectivity. Furthermore, propionylation of veratrole was also carried out by using propionic acid as acylating agent over UDCaT-5 at the same experimental conditions. No acylation product could be obtained since the formation of the carbocation by dehydration of propionic acid did not occur.

3.3. Effect of speed of agitation

The effect of speed of agitation was studied in the range of 800–1200 rpm at a catalyst loading 0.04 g/cm^3 at 80 °C. The mole ratio of veratrole to propionic anhydride was kept at 1:5 (Fig. 5). There was no significant change in the rate and conversion patterns, which was indicative of the absence of external mass transfer resistance. However, all further reactions were carried out at a speed of 1000 rpm. Theoretical calculations were also done to establish that there was absence of external mass transfer resistance. We have given the theoretical development in some of our earlier work [25,28] and a typical calculation is presented here.

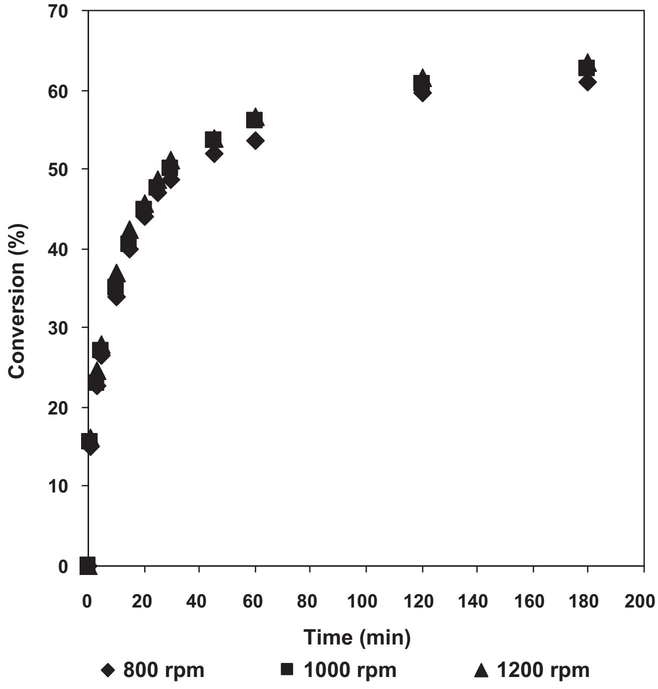


Fig. 5. Effect of speed of agitation on conversion of veratrole. Veratrole: 0.04 mol, propionic anhydride: 0.2 mol, catalyst: UDCaT-5, catalyst loading: 0.04 g/cm^3, temperature: 80 °C.

3.4. Proof of absence of external mass transfer resistance

This is a typical solid–liquid slurry reaction involving the transfer of veratrole, the limiting reactant (A) and propionic anhydride (B) from the bulk liquid phase to the catalyst. It is followed by intra-particle diffusion of the reactant, adsorption of reactants, surface reaction and desorption of products. The influence of external solid–liquid mass transfer resistance must be ascertained before a true kinetic model could be developed.The reaction of veratrole (A) with propionic anhydride (B) produces 3,4-dimethoxypropiophenone (C) and propionic acid (D).

$$A + B \rightarrow C + D \tag{1}$$

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

$$R_A = k_{\text{SL-}A} a_p \{[A_0] - [A_S]\} \tag{2}$$

Similarly, the rate of transfer of B from bulk liquid phase to external surface of the catalyst particle is give by:

$$R_B = k_{\text{SL-}B} a_p \{[B_0] - [B_S]\} \tag{3}$$

$$r_{\text{obs}} = (\text{observed rate of reaction within the catalyst particle}) \tag{4}$$

Here the subscripts “0” and “S” denote the concentrations in bulk liquid phase and external surface of catalyst, respectively. Depending on the relative magnitudes of the external resistance to mass transfer and reaction rates, different controlling mechanisms have been put forward [29]. When the external mass transfer resistance is negligible, then the following inequality holds:

$$\frac{1}{r_{\text{obs}}} >> \frac{1}{k_{\text{SL-}A} a_p [A_0]} \tag{5}$$

and also:

$$\frac{1}{r_{\text{obs}}} >> \frac{1}{k_{\text{SL-}B} a_p [B_0]} \tag{6}$$

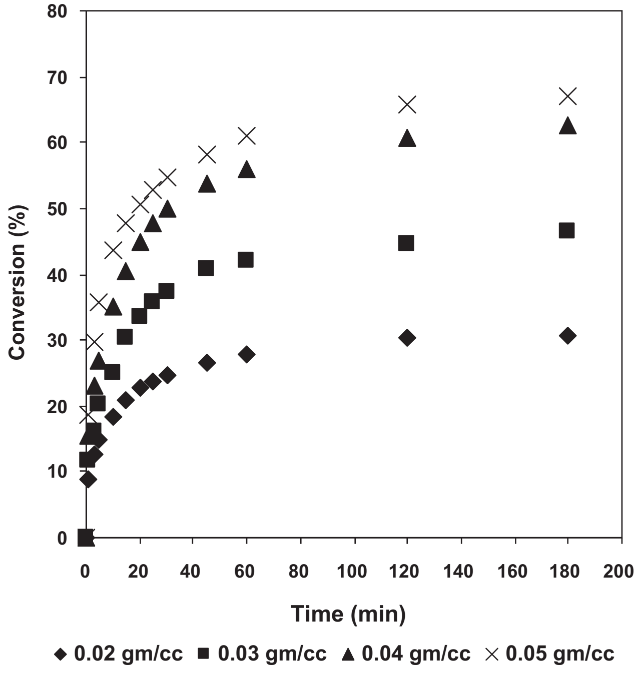


Fig. 6. Effect of catalyst loading on conversion of veratrole. Veratrole: 0.04 mol, propionic anhydride: 0.2 mol, catalyst: UDCaT-5, temperature: 80 °C, Speed of agitation: 1000 rpm.

The observed rate r_{obs} could be given by three types of models wherein the contribution of intra-particle diffusion resistance could be accounted for by incorporating the effectiveness factor η. These models are as follows:

(a) The power law model if there is weak adsorption of reactant species.
(b) Langmuir–Hinshelwood–Hougen–Watson model.
(c) Eley–Rideal mechanism.

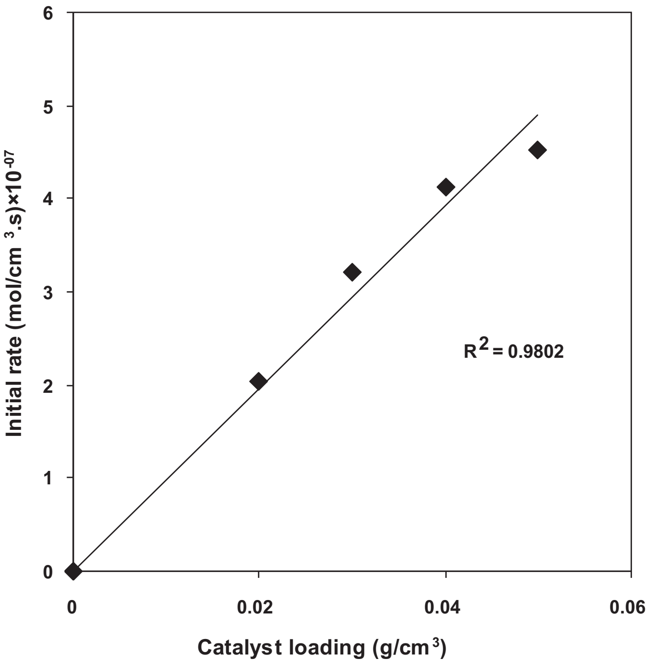


Fig. 7. Plot of initial rate of reaction as a function of catalyst loading in liquid phase.

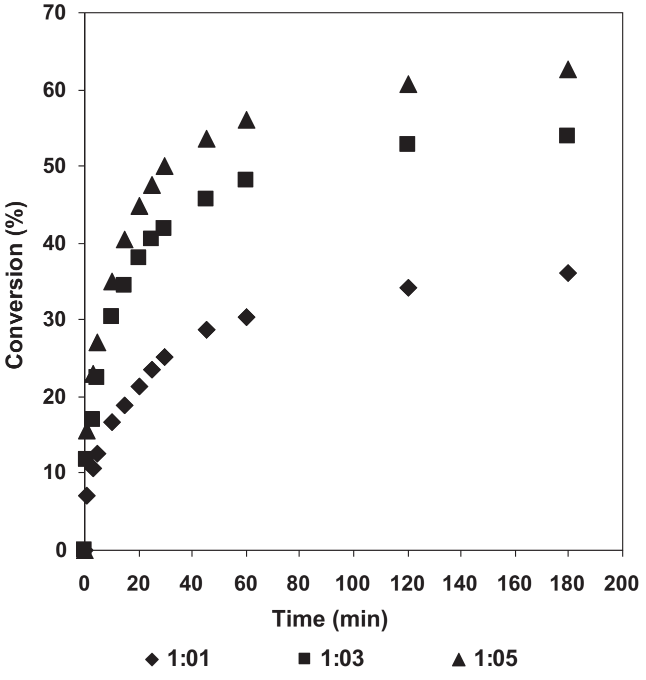


Fig. 8. Effect of mole ratio on conversion of veratrole. Catalyst: UDCaT-5, catalyst loading: 0.04 g/cm^3, temperature: 80 °C, speed of agitation: 1000 rpm.

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

$$a_p = \frac{6w}{\rho_p d_p} \qquad (7)$$

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 system the maximum catalyst loading used was 0.04 g/cm^3 for an average particle size (d_p) of 0.0125 cm. Thus, a_p was calculated as 18.46 cm^2/cm^3. Therefore, the contribution of external mass transfer coefficient could be calculated. The values of liquid-phase diffusivity of the reactants A (veratrole) and B (propionic anhydride), denoted by D_{AB} and D_{BA}, were calculated by using the Wilke–Chang equation at 80 °C as 1.43×10^{-5} cm^2/s and 1.52×10^{-5} cm^2/s, respectively [30]. The solid–liquid mass transfer coefficients for both A and B were calculated from the limiting value of the Sherwood number (e.g. $\mathrm{Sh}_{-A} = k_{SL\text{-}A} d_p / D_{AB}$) of 2. The actual Sherwood numbers are typically higher by order of magnitude in well-agitated system but for conservative estimations a value of 2 was taken. The solid–liquid mass transfer coefficients $k_{SL\text{-}A}$ and $k_{SL\text{-}B}$ values were obtained as 2.30×10^{-3} and 2.44×10^{-3} cm/s. The initial rate of the reaction was calculated from conversion profiles. A typical calculation shows that for a typical reaction, the initial rate of the reaction was calculated as 4.12×10^{-7} mol cm^{-3} s^{-1}. Therefore, by using the appropriate values in (5) and (6) above:

$$\frac{1}{r_{obs}} >> \frac{1}{k_{SL\text{-}A} a_p [A_0]} \text{ and } \frac{1}{k_{SL\text{-}B} a_p [B_0]}$$

i.e. $2.43 \times 10^6 \gg 1.85 \times 10^4$ and 3.49×10^3

The above inequalities also demonstrate that there is absence of resistance to transfer of both A and B from the liquid phase to the external surface of the catalyst particles, and the rate may be controlled either surface reaction or intra-particle diffusion. Therefore, the effect of catalyst loading at a fixed particle size and temperature were studied to evaluate the influence of intra-particle resistance. All further reactions were carried out at agitation speed of 1000 rpm.

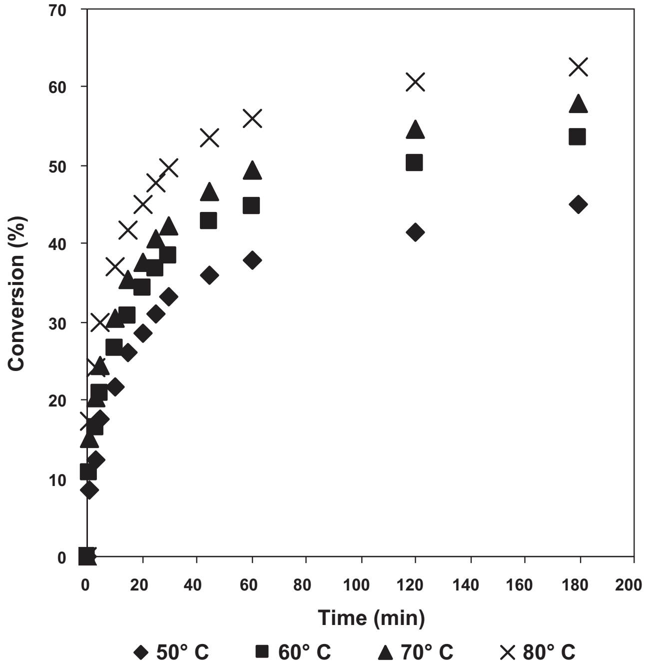


Fig. 9. Effect of temperature on conversion of veratrole. Veratrole: 0.04 mol, propionic anhydride: 0.2 mol, catalyst: UDCaT-5, catalyst loading: 0.04 g/cm^3, speed of agitation: 1000 rpm.

3.5. Effect of catalyst loading

In the absence of external mass-transfer resistance, the rate of reaction is directly proportional to the catalyst loading based on the entire liquid-phase volume. The catalyst loading was varied over range of 0.02–0.05 g/cm^3 on the basis of total volume of the liquid phase. Fig. 6 shows the effect of catalyst loading on the conversion of veratrole. The initial rates of reaction are plotted against catalyst loading in Fig. 7. It demonstrates that the rates are directly proportional to catalyst loading based on the entire liquid phase volume, due to proportional increase in the number of active sites.

For a spherical particle, the particle surface area per unit liquid volume, a_P, is also proportional to w, the catalyst loading per unit liquid volume. It is possible to calculate the values of $[A_s]$ and $[B_s]$. For instance,

$$k_{SL\text{-}A}a_p\{[A_0]-[A_s]\} = r_{\text{obs}} = 4.12\times10^{-7}\text{mol cm}^{-3}\text{ s}^{-1}$$

Thus, when the appropriate values are inserted, it is seen that $[A_S]\approx[A_0]$ and $[B_S]\approx[B_0]$. Thus, any further addition of the catalyst is not going to be of any consequence for external mass transfer.

Further reactions were carried out with 0.04 g/cm^3 catalyst loading used in the standard reaction.

3.6. Proof of absence of intra-particle resistance

An absence of intra-particle mass transfer resistance could be well proved from the experimental data with different catalyst particle sizes. But it can be done only with those catalysts, which do not have uniform particle size. UDCaT-5 catalyst is sulfate promoted zirconia catalyst and its mean particle size was 0.0125 cm.

According to the Weisz Prater criterion, the parameter C_{WP}, which represents the ratio of the intrinsic reaction rate to intra-particle diffusion rate, can be evaluated from the knowledge of observed rate (r_{obs}), 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.

(i) If $C_{\text{WP}} = r_{\text{obs}}\rho_p R_p^2/D_e[A_S] >> 1$, then the reaction is limited by severe intra-particle diffusion resistance.
(ii) If $C_{\text{WP}} \ll 1$, then the reaction is intrinsically kinetically controlled.

The effective diffusivity of veratrole ($D_{e\text{-}A}$) inside the pores of the catalyst was obtained from the bulk diffusivity (D_{AB}), porosity (ε) and tortuosity (τ) as 1.91×10^{-6} cm^2/s, where $D_{e\text{-}A} = D_{AB}\ (\varepsilon/\tau)$. In the present case, the value of C_{WP} was calculated as 0.0011 from the initial observed rate. Since C_{WP} is much less than 1, the reaction is intrinsically kinetically controlled. Further proof of the absence of the intra-particle diffusion resistance was obtained through the study of the effect of temperature which will be discussed later.

3.7. Effect of mole ratio

The effect of mole ration of veratrole to propionic anhydride was studied at 1:1, 1:3 and 1:5 by keeping the catalyst loading per unit volume constant. The conversion of veratrole was found to increase with an increase in concentration of propionic anhydride (PA) (Fig. 8). It leads to a higher concentration of electrophile PA to react with veretrole, resulting in higher reaction rate and conversion of veratrole. Therefore, all reactions were studied by using a veratrole to propionic anhydride mole ratio of 1:5.

3.8. Effect of temperature

The effect of temperature on conversion was studied under otherwise similar conditions at 50, 60, 70 and 80 °C. It was observed that the conversion increased with temperature (Fig. 9). This would suggest a kinetically controlled mechanism. The initial rates of reaction were calculated at different temperatures and the Arrhenius plot was made to determine the energy of activation (Fig. 10). It was found to be 7.32 kcal/mol, which is an indication of the overall rate being controlled by intrinsic kinetics.

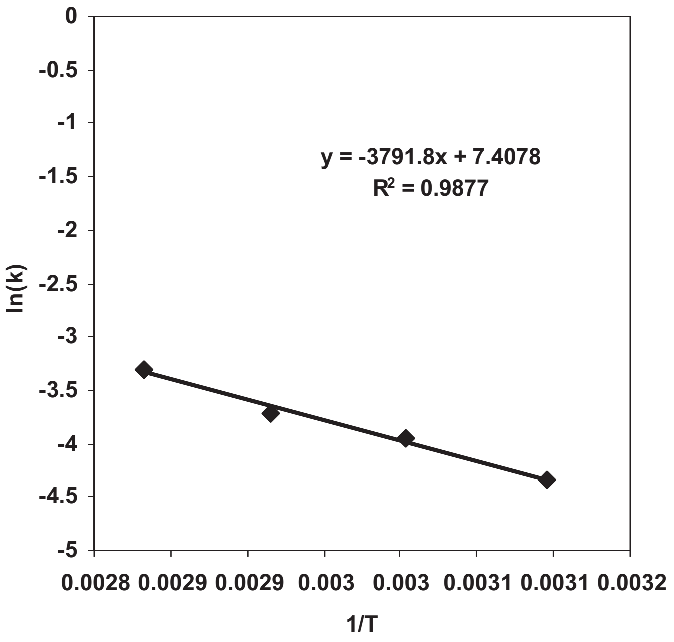


Fig. 10. Arrhenius plot (plot of ln *k* vs 1/*T*). Veratrole: 0.04 mol, propionic anhydride: 0.2 mol, catalyst: UDCaT-5, catalyst loading: 0.04 g cm^{-3}, speed of agitation: 1000 rpm.

3.9. Reusability of catalyst

The catalyst reusability was studied three times, including the use of fresh catalyst. After each run, the catalyst was filtered, washed with methanol, 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. Although the catalyst was washed with methanol after filtration to remove all adsorbed reactants and products, there was still a possibility of retention of some amount of adsorbed reactants and products which might cause the blockage of active sites of the catalyst. The actual amount of catalyst used in the next batch, was almost 5% less than the previous batch. There is only a marginal decrease in conversion. When fresh amount of catalyst was added to make up for the losses, there was no reduction in conversion and yields, which showed that the catalyst was stable.

3.10. Development of kinetic model

The above results were used to build a kinetic model. The reaction involves two organic phase reactants, *A* (veratrole), *B* (propionic anhydride), the desired product *C* (3,4-methoxypropiophenone) and *D* (co-product propionic acid). Since *A* and *B* are liquid phase reactants, they need to diffuse to the interior surface of the catalyst. The different steps involved in this process are according to the Eley–Rideal mechanism, which was found to hold for acid catalyzed acylation reactions [25,31].

The first step involves the formation of carbocation by the adsorption of propionic anhydride on a catalytic site (*S*):

$$\underset{(B)}{(\mathrm{CH_3CH_2CO})_2\ \mathrm{O}} + \underset{(S)}{\mathrm{H}^+} \underset{k_a}{\overset{k_a}{\rightleftarrows}} \underset{(BS)}{\mathrm{CH_3CH_2C^+O}} + \underset{(D)}{\mathrm{CH_3CH_2COOH}} \quad (8)$$

The rate of chemisorption of *B*:

$$-r_B = k_B C_B C_S - k_{B'} C_{BS} C_D \quad (9)$$

$-r_B = 0$, at equilibrium (quasi equilibrium)

$$k_B C_B C_S = k'_B C_{BS} C_D \quad (10)$$

Since $K_B = k_B/k'_B$

$$C_{BS} = K_B \frac{C_B C_S}{C_D} \quad (11)$$

Now the reaction between the adsorbed *B* as *BS* and liquid-phase reactant *A* takes place as follows,

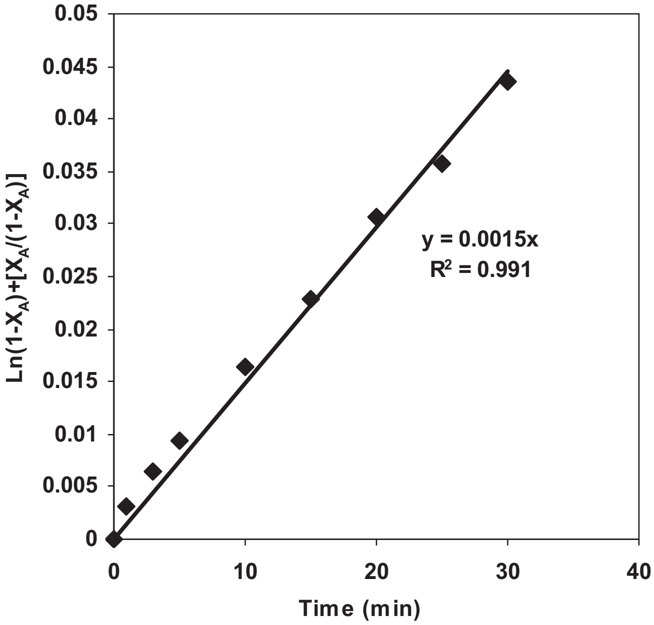


Fig. 11. Plot of $\ln(1-X_A)+[X_A/(1-X_A)]$ vs time for $M = 1$.

where k_{SR} is the reaction rate constant.

The rate of reaction of veratrole per unit liquid volume is given by

$$-\frac{dC_A}{dt} = k_{SR} C_A C_{BS} \quad (12)$$

After substitution for C_{BS}.

$$-\frac{dC_A}{dt} = k_{SR} C_A \frac{K_B C_B C_S}{C_D} = (k_{SR} K_B) \frac{C_B C_A C_S}{C_D} \quad (13)$$

The total side balance is as follows,

$$C_t = w = C_{BS} + C_{AS} + C_S \quad (14)$$

where *w* is the catalyst loading.

when $C_{AS} = 0$, $w = C_{BS} + C_S$

$$C_S = \left(\frac{w}{1 + K_B C_B / C_D} \right) \quad (15)$$

After substituting the C_S in Eq. (13),

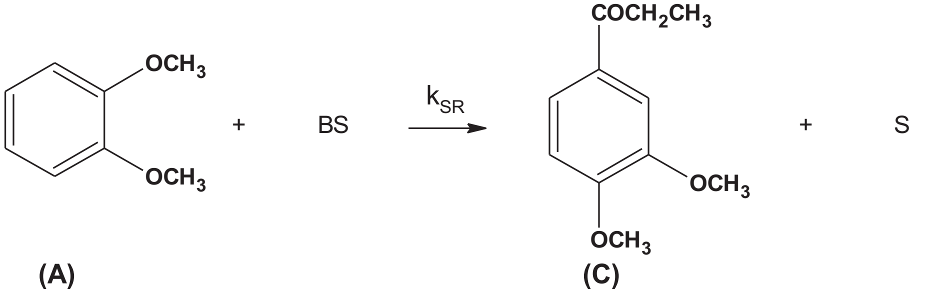
$$-\frac{dC_A}{dt} = \frac{k_{SR} K_B w C_B C_A}{(C_D + K_B C_B)} = r_A \quad (16)$$

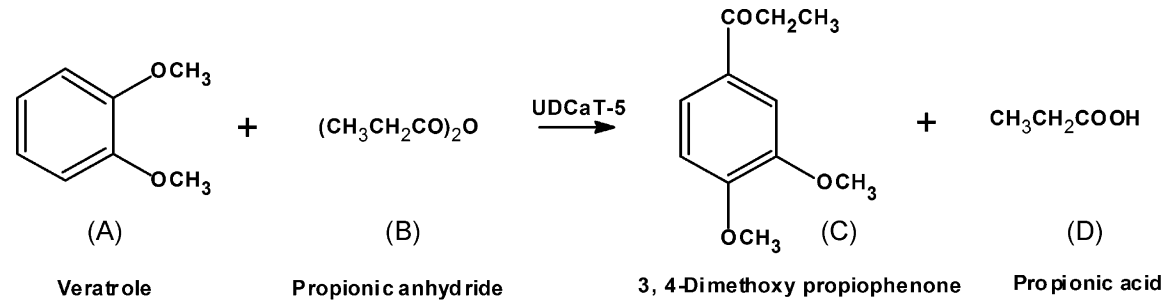
$$C_A = C_{A_0}(1 - X_A) \quad (16a)$$

$$C_B = C_{B_0} - C_{A_0} X_A = C_{A_0}(M - X_A) \quad (16b)$$

$$C_D = C_{A_0} X_A \quad (16c)$$

where $C_{B_0}/C_{A_0} = M$, initial mole ratio of propionic anhydride to veratrole X_A = fractional conversion of *A*. Substituting in terms of X_A and integrating, the following equations are obtained.





Scheme 1. Propionylation of veratrole to 3,4-dimethoxypropiophenone using UDCaT-5 as novel solid acid catalyst.

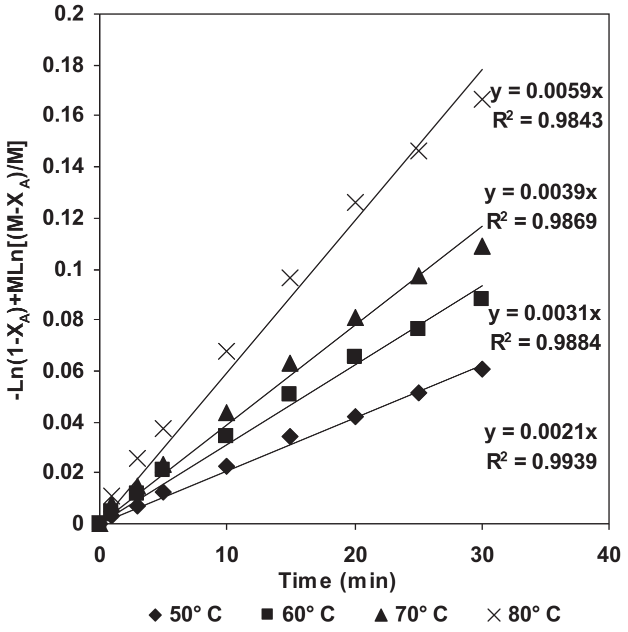


Fig. 12. Plot of $-\ln(1-X_A)+M\ln[(M-X_A)/M]$ vs time for $M \neq 1$.

Case (a): for $M=1$,

$$\ln(1-X_A)+\frac{1}{(1-K_B)}\frac{X_A}{(1-X_A)}=\frac{k_{SR}K_Bwt}{(1-K_B)} \tag{17}$$

Case (b): for $K_B \ll 1$

$$\ln(1-X_A)+\frac{X_A}{(1-X_A)}=k_{SR}K_Bwt \tag{18}$$

Case (c): $M \neq 1$,

$$-\ln(1-X_A)+\left[\frac{M}{K_B(M-1)+1}\right]\ln\left[\frac{M-X_A}{M}\right]=\left[\frac{k_{SR}K_B(M-1)wt}{K_B(M-1)+1}\right] \tag{19}$$

Case (d): for very small values of K_B, $K_B(M-1)+1 \approx 1$

$$-\ln(1-X_A)+M\ln\left[\frac{M-X_A}{M}\right]=k_{SR}K_B(M-1)wt \tag{20}$$

These models were validated against the experimental data.

It was found that the adsorption of B was very weak ($K_B \ll 1$) and thus Eq. (18) for $M=1$ (Fig. 11) and Eq. (20) for $M \neq 1$ (Fig. 12) fit the data very well (Scheme 1).

4. Conclusion

The Friedel–Crafts acylation of veratrole with propionic anhydride was studied at 80 °C over a variety of solid acid catalysts such as UDCaT-4, UDCaT-5 and UDCaT-6. UDCaT-5 was the most active, selective, stable and reusable catalyst. It gave 100% selectivity towards the desired product 3,4-dimethoxypropiophenone. The effects of various parameters on the rates over UDCaT-5 were discussed. A kinetic model for the reaction mechanism was successfully developed. It follows Eley–Rideal type of mechanism, wherein the chemisorbed propionic anhydride generates a carbocation and propionic acid, and carbocation reacts with veratrole from the liquid phase within the pore space. The energy of activation was found to be 7.32 kcal/mol.

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