

Selective Claisen rearrangement of allyl-2,4-di-*tert*-butylphenyl ether to 6-allyl-2,4-di-*tert*-butylphenol catalysed by heteropolyacid supported on hexagonal mesoporous silica

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Abstract

The Claisen rearrangement of allyl phenyl ethers results into valuable products for fragrance, flavours, food, pharmaceuticals and intermediate industries and is typically initiated by using very high temperatures, normally beyond 200 °C. Homogeneous acid catalysts are also used for this rearrangement, which could be replaced profitably by using eco-friendly solid acids. The Claisen rearrangement of allyl-2,4-di-*tert*-butylphenyl ether to 6-allyl-2,4-di-*tert*-butylphenol was accomplished by employing the various solid acid catalysts such as K-10 clay, sulphated zirconia, 20% w/w dodecatungstophosphoric acid (DTP)/hexagonal mesoporous silica (HMS), and 20% w/w DTP/K-10. A 20% w/w DTP/HMS was found to be very active and also stable without any deactivation with 100% atom economy towards 6-allyl-2,4-di-*tert*-butylphenol, which is commercially a very valuable product. A systemic investigation of the effect of various operating parameters is done. Furthermore, a mathematical model is developed to describe the reaction kinetics, which is validated with experimental results. The results are novel.

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Keywords: Claisen rearrangement; Allyl-2,4-di-*tert*-butylphenyl ether; 6-Allyl-2,4-di-*tert*-butylphenol; Heteropolyacid; Dodecatungstophosphoric acid; K-10 clay; Hexagonal mesoporous silica; Sulfated zirconia; Mesoporous catalyst; Selectivity; Kinetics

1. Introduction

The Claisen rearrangement is primarily used as one of the favourite carbon–carbon bond forming reactions in organic synthesis [1], due to the simplicity of protocol and high degree of stereoselectivity and functional group reorganization. The aromatic Claisen rearrangement is accompanied by a rearomatization and is generally a thermally initiated reaction. The initial [3,3] step in the Claisen rearrangement of allyl aryl ether gives an *ortho*-dienone, which rapidly enolizes to an *o*-allylphenol. However, if the *ortho* position already has a substituent, then a second [3,3] step followed by enolization leads to the *para*-Claisen rearrangement. When the *ortho*

position is substituted, rearomatization cannot take place. The allyl group must first undergo a Cope rearrangement to the *para* position before tautomerization is possible. The *ortho*-Claisen rearrangement predominates in unexceptional cases, but the *para*-process can take over even when both *ortho* and *para* positions are free. Thus, the Claisen rearrangement is used to make *o*-allyl phenols, which are precursors to a variety of natural products including chromones and coumarones [2–4]. Several catalysts such as Lewis acids, Bronsted acids, bases and transition metal complexes have been used to study Claisen rearrangement [5]. In the context of green chemistry, it is desirable that highly polluting homogeneous catalysts should be replaced by heterogeneous catalysts [6].

The Claisen rearrangement of allyl-2,4-di-*tert*-butylphenyl ether to 6-allyl-2,4-di-*tert*-butylphenol is industrially a valuable reaction and the novelty of this reaction is reported here. 6-Allyl-2,4-di-*tert*-butylphenol is used as antioxidant,

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Nomenclature

| | |
|------------|---|
| C_{AS} | concentration of adsorbed species A (mol/cm ³) |
| C_S | concentration of vacant sites (mol) |
| C_T | total concentration of sites (mol) |
| K_A, K_B | adsorption constant for A and B, respectively (cm ³ /mol) |
| k_{SR} | reaction rate constant (cm ³ /mol g-cat min) |
| k_1 | Pseudo first-order rate constant (cm ³ /g-cat min) |
| k_o | frequency factor (cm ³ /g-cat min) |
| $-r_A$ | rate of reaction of A (mol cm ⁻³ min ⁻¹) |
| S | vacant site |
| X_A | fractional conversion of allyl-2,4-di- <i>tert</i> -butylphenyl ether |
| w | catalyst loading (g/cm ³ liquid phase) |

Subscripts

| | |
|---|--|
| A | allyl-2,4-di- <i>tert</i> -butylphenyl ether |
| B | 6-allyl-2,4-di- <i>tert</i> -butylphenol |

cross linking agent in polymers and also reactive diluent in UV-curable coating composition. It is also used in perfumes, flavours, and particularly in the formulation of products such as soaps, detergents, air fresheners, as well as in cosmetic materials. Use of solid acids has been made for Claisen rearrangement including Al-MCM-41 [7], H-FAU and H-MOR [8,9], β -zeolite [10], mesoporous silica [11], and bentonite [12] which have been used for allyl phenyl ether as the reactant. Recently we have studied the Claisen rearrangement of allyl-4-methoxyphenyl ether using a zirconia modified catalyst, UDCaT-5 [13]. However, there is no report on the Claisen rearrangement of allyl-2,4-di-*tert*-butylphenyl ether using solid acids.

Efficacy of supported heteropolyacids on clays and mesoporous materials for a variety of acid catalyzed reactions has been studied by us in several reactions. Dodecatungstophosphoric acid (DTP) is considered the strongest acid among heteropolyacids (HPA). However, its low surface area (<5 m²/g) and high solubility in polar solvents limit its potential catalytic applications and different supports have been used [14]. Syntheses of well-ordered mesoporous inorganic solids with pores of diameter 20–100 Å have opened a new field in advanced material research and are increasingly being modified to bring into functionality or simply as supports [15–17].

Attempts were made to immobilize HPAs on different oxide supports [14,17–28] or convert them into their corresponding alkali metal salts [19]. The supporting of HPAs on a suitable support overcomes the disadvantage of HPAs and lends greater accessibility to acid sites resulting in high activity and also stability. The interaction level of HPA with the support controls both acid structure and mobility. Various supports like silica [20,21] alumina [22], activated carbon

[23,24], and MCM-41 [25] have been used for supporting HPAs. A number of HPAs supported on K-10 clay were reported as novel catalysts by our laboratory [14,26] and 20% dodecatungstophosphoric acid on K-10 has been found to be a very efficient catalyst for a number of reactions [26,29–36].

The current study deals with the Claisen rearrangement of allyl-2,4-di-*tert*-butylphenyl ether to 6-allyl-2,4-di-*tert*-butyl phenol using several solid acids including kinetic modelling.

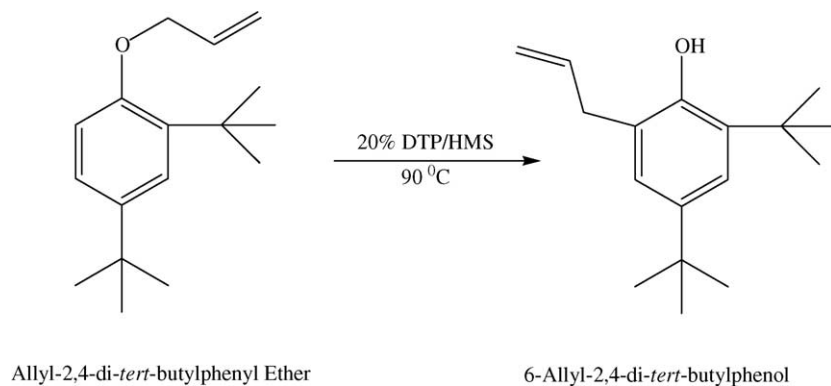
2. Experimental

2.1. Chemicals and catalysts

All chemicals and solvents used in this study were commercially available and used without further purification. Chlorobenzene, zirconium oxychloride, aqueous ammonia solution, sulfuric acid, and dodecatungstophosphoric acid (DTP) all of AR grade were obtained from M/s s.d. Fine Chemicals Pvt. Ltd., Mumbai, India. Dodecylamine, and hexadecylamine were obtained from Spectrochem Ltd., Mumbai. K-10 clay and tetraethylorthosilicate (TEOS) were obtained from Fluka, Germany. The catalysts used for the reaction were dried at 110 °C for 4 h before use. A 20% w/w DTP/K-10 [26] and sulfated zirconia [37] were prepared by a well established procedure in our laboratory. A 20% w/w DTP/HMS was synthesized by a procedure of Yadav and Manyar [38]. Allyl-2,4-di-*tert*-butylphenyl ether was synthesized in our laboratory from 2,4-di-*tert*-butylphenol and allyl bromide by using phase transfer catalysis [39].

2.2. Preparation of 20% w/w DTP/HMS

Hexagonal mesoporous silica (HMS) was synthesized by the neutral S⁰I⁰ templating route, proposed by Tanev and Pinnavaia [40]. In a typical preparation, tetraethylortho silicate (TEOS) was added under vigorous stirring to a solution of dodecylamine (DDA) in ethanol and de-ionized water to obtain a gel of composition 1.0 TEOS:0.27 dodecylamine:9.09 EtOH:50.8 H₂O. After aging for 18 h at ambient temperature, a templated silica molecular sieve with short-range hexagonal morphology was recovered. Template removal was achieved by calcination at 550 °C in air. A 20% w/w DTP/HMS was prepared by incipient wetness technique; 2 g of dry DTP (dodecatungstophosphoric acid) was weighed accurately. This was dissolved in 8 ml of methanol. The solution was added in small aliquots of 1 ml each time to 8 g of HMS with constant stirring with a glass rod and kneading it properly. The solution was added at time intervals of 2 min. Initially on addition of the DTP solution, HMS was in a powdery form but on complete addition it formed a paste. The paste on further kneading for 10 min resulted in a free flowing powder. The catalyst was dried at 120 °C and subsequently calcined at 285 °C for 3 h.

Scheme 1. Claisen rearrangement of allyl-2,4-*tert*-butylphenyl ether.

2.3. Experimental setup

The experimental setup consisted of a 3 cm i.d. fully baffled mechanically agitated glass reactor of 50 ml capacity, equipped with four baffles and a six-bladed turbine impeller. The entire reactor assembly was immersed in a thermostatic water bath, which was maintained at a desired temperature with an accuracy of ± 1 °C.

A typical reaction mixture consisted of 0.01 mol of allyl-2,4-di-*tert*-butylphenyl ether in 10 cm³ of chlorobenzene as a solvent with a catalyst loading of 0.1 g/cm³ at a agitation speed of 1000 rpm at 90 °C.

2.4. Analysis and isolation of product

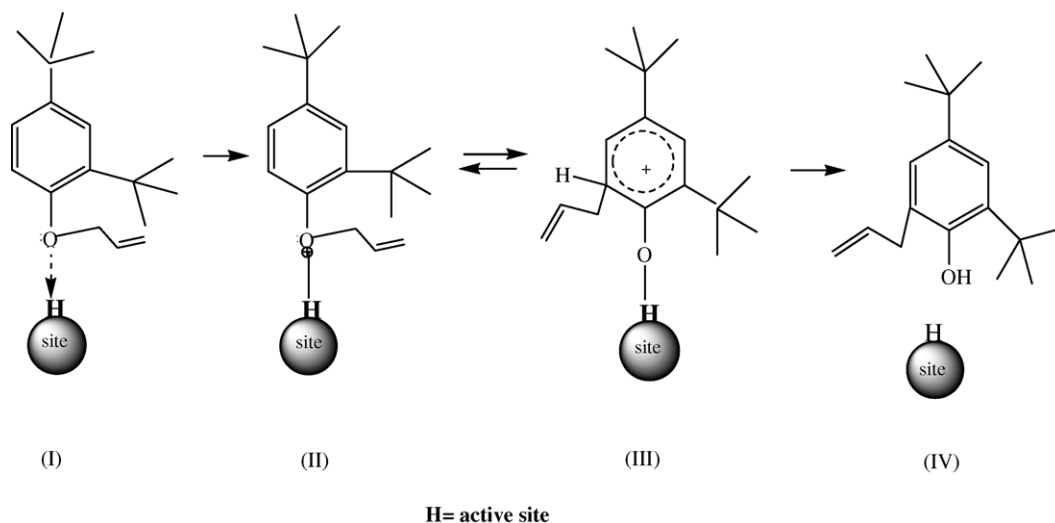
The analysis was done on a gas chromatograph (Chemito-8610) equipped with a flame ionisation detector. A (3.25 mm \times 2 m) long stainless steel column packed with 10% SE-30 supported on chromosorb-WHP was used for the analysis. The injector and detector were kept at 300 °C. The oven temperature was programmed from 130 °C (0.5 min) up

to 280 °C with a ramp rate of 10 °C min⁻¹. Synthetic mixtures were used to calibrate and quantify the data.

For the isolation of the product, the reaction mixture was filtered to remove the catalyst DTP/HMS for further reuse and the solution was treated with aqueous NaOH to remove the phenol as phenate salt, which on acidification gave the product. The isolated product 6-allyl-2,4-di-*tert*-butylphenol (B.P. 76 °C at 0.15 mmHg) was distilled and confirmed by GC-MS (Perkin-Elmer Clarius Model 500) by using BPX-1 capillary column (0.25 mm \times 30 m) packed with methyl polysiloxane. The reaction is shown in Scheme 1.

2.5. Mechanism of the Claisen rearrangement using 20% w/w DTP/HMS

The mechanism of Claisen rearrangement using 20% w/w DTP/HMS, with general acidic site H is proposed in Scheme 2. According to this mechanism, the oxygen of the ether having a lone pair of electrons is chemisorbed on the acidic site and then the allyl group migrates to the most



Scheme 2. Reaction mechanism on 20% w/w DTP/HMS.

favourable *ortho* position through intramolecular rearrangement. The product is desorbed thereby freeing the site for next catalytic cycle.

3. Results and discussion

3.1. Evaluation of catalyst stability

The ordered mesoporous silica molecular sieve with large surface silanol groups is catalytically inert. The surface acidity of HMS was due to the DTP. However, it was important to establish the exact nature of interaction between DTP and silica surface. If DTP was physically adsorbed on HMS surface, then the catalyst would not be reused because of leaching out of DTP into the reaction mixture. It was observed that the DTP/HMS showed a consistent activity up to a minimum of three runs, which suggested that DTP was chemically bonded to the support. For further confirmation, the stability was evaluated by the characteristic heteropoly blue colour test [30]. HPA solutions develop blue colour when reacted with a mild reducing agent like ascorbic acid. This property was used for quantitative determination of leaching, if any. Five grams of 20% w/w DTP/HMS was refluxed in 25 ml of methanol with vigorous stirring for 1 h. Five milliliters aliquot of the refluxing solution was drawn to which 2 ml of 10% ascorbic acid solution was added. The solution remained clear and colourless and there was no development of the blue colour which otherwise is an instantaneous phenomenon in authentic HPA solutions. Such a test was also done in chlorobenzene to find that there was no leaching of DTP from HMS. The above test was repeated for the used catalyst as well to confirm the absence of leaching.

It was found that when the catalyst was filtered from the solution and the reaction was continued, there was no further reaction, which again established that the catalyst was stable.

3.2. Efficacies of various catalysts

In the case of a bulky reactant like allyl-2,4-di-*tert*-butylphenyl ether and a bulkier product 2-allyl-4-di-*tert*-butylphenol, the type of acidity, its strength and the pore structure would matter greatly. As regards the pore structure, the pore size distribution should be as narrow as possible and in mesoporous range, with high co-ordination number connecting the bulges to throats. Thus, a variety of solid acids having mesoporous structure were considered including 20% w/w DTP/HMS, K-10 clay, 20% w/w DTP/K-10 and sulfated zirconia (SZ). A 0.1 g/cm³ loading of catalyst based on the organic volume of the reaction mixture was employed at 90 °C at a speed of 1000 rpm. It was found that 20% w/w DTP/HMS showed higher conversions compared to other catalysts (Fig. 1). The reactant and the product are bulky molecules and require bigger pores to overcome intra-particle diffusion problems. In the case of K-10 clay and sulphated zirconia, there is a bimodal distribution of pore

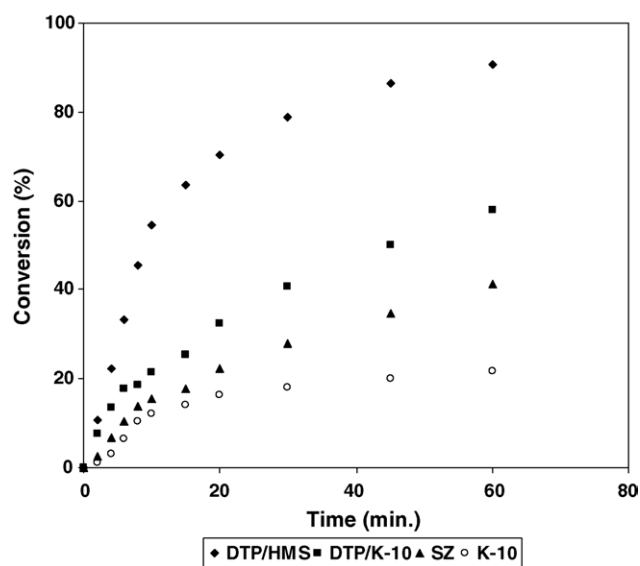


Fig. 1. Effect of different catalyst. Allyl-2,4-di-*tert*-butylphenyl ether 0.01 mol, chlorobenzene 10 cm³, catalyst 0.1 g/cm³, temperature 90 °C, speed of agitation 1000 rpm.

sizes and some pores are in the mesoporous region and many in microporous region. Sulfated zirconia is a superacid. In the case of K-10 clay and sulphated zirconia, the bulky molecules trapped in some pore junctions could render a large network inaccessible thereby reducing the activity. On the contrary DTP/HMS provides largely Bronsted acidic sites with uniform mesopores (~3.3 nm) and is an efficient catalyst. It was found that there was no other byproduct and the reaction was facile at much lower temperatures also. Thus, DTP/HMS was found to be a better catalyst. The large surface area of silica molecular sieves allows Keggin anions to disperse uniformly on the surface and it constitutes a stable solid acid catalyst system. An important potential benefit of supporting dodecatungstophosphoric acid on silica molecular sieve is enhanced thermal stability, which is in agreement of previous work. HPAs were found to retain their Keggin type structure when impregnated on silica provided its contents are greater than 2% w/w [38]. There was thus a synergism between HMS and DTP in the supported form. However, an independent study was undertaken to evaluate the stability of the catalyst under experimental conditions and it was found that there was no leaching of the HPA and the catalyst was stable, as was found earlier in acylation reactions [38]. Thus, further experiments were conducted with 20% w/w DTP/HMS. A brief characterization of this catalyst is presented.

3.3. Catalyst characterization

A 20% w/w DTP/HMS was completely characterized by FT-IR, XRD, SEM, BET surface area, and the details were published by us [38]. Only a few salient features are reported here. The framework IR spectrum of the catalyst exhibits bands at 3450.1, 1652.6, 1092.5, 990.7, 893.4, 817.5,

466.2 cm^{-1} . The bands coincide with those reported in the literature for the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [41–43]. The bands of the DTP-supported on HMS appear at 1092.5, 990.7 and 893.4 cm^{-1} . The presence, in the IR spectra of catalytic samples, of the 817 cm^{-1} band is due to a Si–O bending mode, $\nu_{\text{B}}(\text{O–H})$. The sharp peak in the region 1600–1700 cm^{-1} indicates the presence of H_3O^+ (Bronsted acidity). In addition, these materials exhibit a strong 3450 cm^{-1} band, which is associated with silanol group O–H stretching vibrational mode, $\nu_{\text{S}}(\text{O–H})$ [41–43]. This band is much broad as compared to the one observed in case of zeolite molecular sieves which is due to presence of physisorbed and chemisorbed surface water molecules.

The X-ray diffraction patterns of authentic HMS as well as 20% w/w DTP/HMS were recorded. The XRD patterns of these materials do not contain any sharp reflections but only a broad diffuse band similar to that of amorphous materials. The XRD patterns for DTP supported on silica were similar to those of the corresponding HMS. In particular, no crystalline phase could be detected in case of DTP supported on silica. This could be attributed to the uniform distribution of keggian anion ($\text{PW}_{12}\text{O}_{40}^{3-}$) in the non-crystalline form because of the interaction with surface of silica molecular sieve. These materials are, hence, completely amorphous without any long range order.

Scanning electron microscopy shows that the average particle size is in the range of 2–4 μm . As is generally observed in the case of materials synthesized by sol–gel technique, these catalytic samples show particles of irregular morphology, which are fairly uniform in size.

Characteristic nitrogen BET surface area is 908 m^2/g . As observed from BJH adsorption pore size distribution, a major part of the surface area is contributed by pores with a diameter characteristic of pores ranging from 17.1 to 33.0 \AA . There is also a significant part due to mesopores ranging from 33.0 to 67.0 \AA . The catalyst is essentially mesoporous. Some of the textural characteristics of these catalytic samples are given in Table 1.

3.4. Effect of speed of agitation

The effect of speed of agitation was studied in the range of 800–1200 rpm as shown in Fig. 2 for 20% w/w DTP/HMS, under otherwise similar conditions. It was observed that there was no change in the rate of reaction and conversion beyond a speed of 1000 rpm, thereby indicating that there was no resistance due to external solid–liquid mass transfer.

Table 1

Textural characteristics of 20% w/w DTP/HMS

| Sample | 20% w/w DTP/HMS |
|--|-----------------|
| Single point surface area | 840 |
| BET surface area (m^2/g) | 909 |
| Langmuir surface area (m^2/g) | 1264 |
| BJH adsorption cumulative pore volume (cm^3/g) | 0.538 |
| Average pore diameter (4 V/A) (\AA) | 26 |

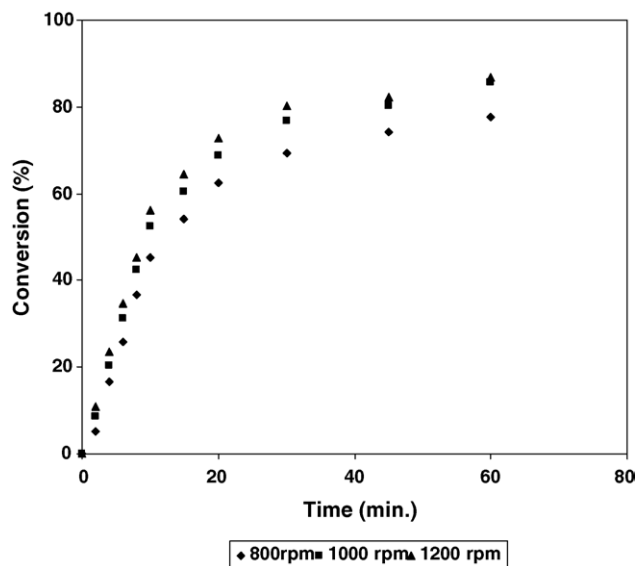


Fig. 2. Effect of speed of agitation. Allyl-2,4-di-*tert*-butylphenyl ether 0.01 mol, chlorobenzene 10 cm^3 , 20% (w/w) DTP/HMS 0.1 g/cm^3 , temperature 90 $^\circ\text{C}$.

In further experiments, the speed was maintained at or above 1000 rpm.

3.5. Effect of catalyst loading

In the absence of external 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 0.025–0.15 g/cm^3 on the basis of the total volume of the reaction mixture. Fig. 3 shows the effect of catalyst loading on the conversion of allyl-2,4-di-*tert*-butylphenyl ether. It indicates that as the catalyst loading

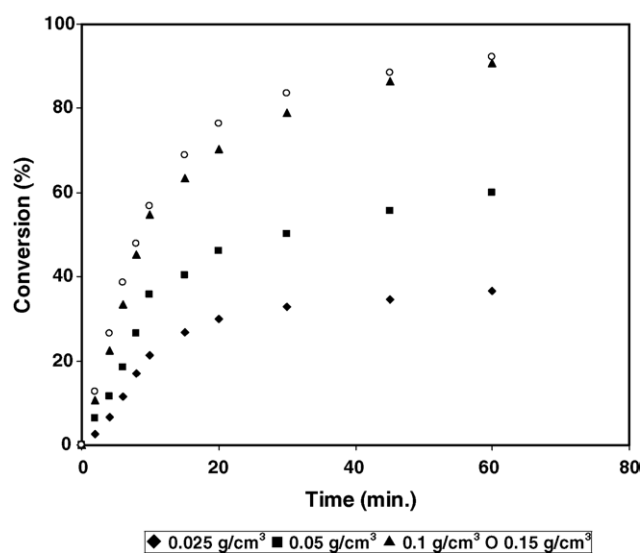


Fig. 3. Effect of catalyst loading. Allyl-2,4-di-*tert*-butylphenyl ether 0.01 mol, chlorobenzene 10 g/cm^3 , temperature 90 $^\circ\text{C}$, speed of agitation 1000 rpm.

is increased, the conversion of allyl-2,4-di-*tert*-butylphenyl ether increases, which is due to proportional increase in the number of active sites. At higher catalyst loading, the number of active sites available for reaction were much larger than required and therefore there was no more increase in the rate. Therefore, all further experiments were carried out at 0.1 g/cm^3 of catalyst loading. Further, there was no intraparticle diffusion limitation, which was established by invoking the Wiesz–Prater criterion based on initial rates of reaction, particle size and effective diffusivity of the substrate at 90°C . This is omitted for sake of brevity.

3.6. Effect of the concentration of allyl-2,4-di-*tert*-butylphenyl ether

The concentration of allyl-2,4-di-*tert*-butylphenyl ether was varied by taking 0.0025 – 0.02 mol of the substrate keeping the total volume of reaction mass as constant. It was observed that as the concentration increases the conversion decreases (Fig. 4). The initial rate of reaction increases linearly with concentration. This suggested a first-order dependence on catalyst concentration and formed a basis for development of kinetics.

3.7. Effect of temperature

The effect of temperature on the rate of reaction was studied by conducting the reaction at 60 , 70 , 80 , 90 and 100°C under otherwise similar condition as shown in Fig. 5. The conversion of allyl-2,4-di-*tert*-butylphenyl ether was found to increase substantially with increasing temperature up to 100°C .

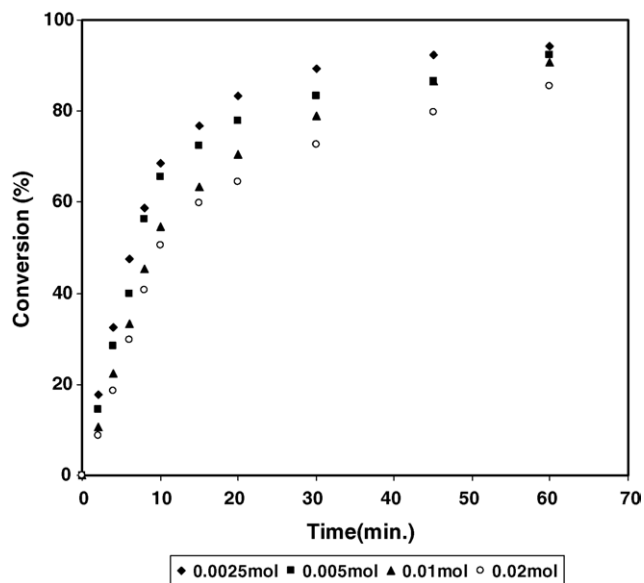


Fig. 4. Effect of concentration of allyl-2,4-di-*tert*-butylphenyl ether. Chlorobenzene 10 cm^3 , temperature 90°C , 20% (w/w) DTP/HMS, 0.1 g/cm^3 , speed of agitation 1000 rpm.

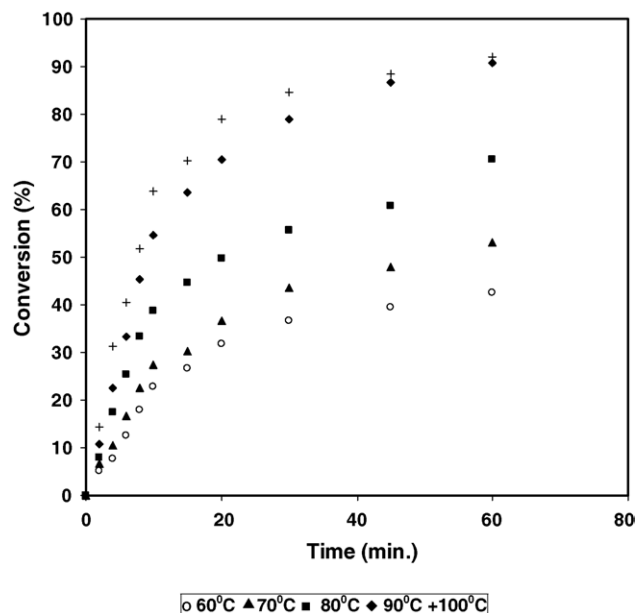


Fig. 5. Effect of temperature. Allyl-2,4-di-*tert*-butylphenyl ether 0.01 mol , chlorobenzene 10 cm^3 , 20% (w/w) DTP/HMS 0.1 g/cm^3 , speed of agitation 1000 rpm.

3.8. Reusability of catalyst

The catalyst reusability of 20% w/w DTP/HMS was studied four times, including the use of fresh catalyst (Fig. 6). The catalyst was filtered, washed with chlorobenzene and subsequently heated at 285°C for 2 h before being reused in subsequent batches. This reactivation was done to remove the molecules adsorbed on active sites from the catalyst surface. In the presence of the fresh catalyst, the conver-

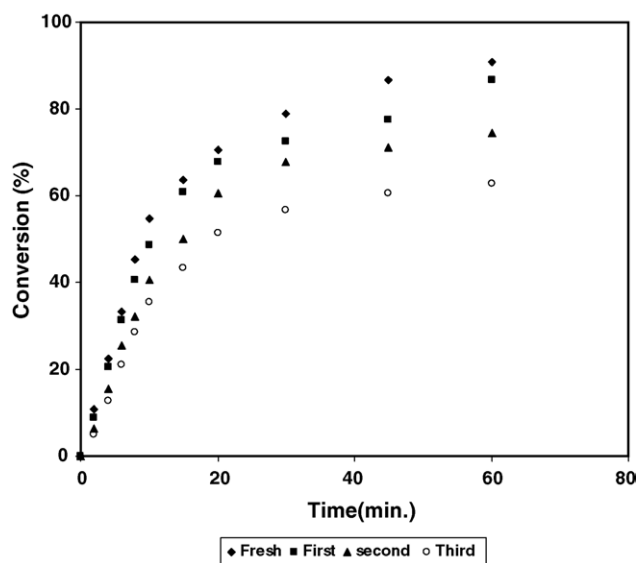


Fig. 6. Reusability of catalyst (no make-up). Allyl-2,4-di-*tert*-butylphenyl ether 0.01 mol , chlorobenzene 10 cm^3 , 20% (w/w) DTP/HMS 0.1 g/cm^3 , temperature 90°C , speed of agitation 1000 rpm.

sion of allyl-2,4-di-*tert*-butylphenyl ether was 90.7%. During the fourth run the conversion decreased to 62.7% while the selectivity towards 6-allyl-4-*tert*-butylphenol remained 100%. During intense agitation, there was an attrition of catalyst and during filtration, some was lost. Since no make-up was done, there was a drop in conversion. In order to see whether there was no any loss of activity due to adsorbed reactant or product, the catalyst was washed with chlorobenzene, and a make-up was added to observe that the activity was maintained within 5% of the original value on repeated use. Thus, the catalyst was stable, active and reusable.

3.9. Effect of different solvents

The effect of different solvents on the rate of the reaction was studied. It was observed that in case of toluene and mixed xylenes, the alkylation reaction of the substrate with the solvent takes place by migration of allyl carbonium ion from allyl-2,4-di-*tert*-butylphenyl ether to the activated aromatic rings of the solvent to form allylated toluene and xylenes. This was due to the high acidity of 20% w/w DTP/HMS and it results in to the decrease in selectivity of desired product. Chlorobenzene was found to be the best solvent, without any byproducts.

3.10. Reaction kinetics

It is known that in the Claisen rearrangement the rate of reaction follows first-order kinetic behaviour for thermal reactions [43,44]. In the absence of any mass transfer limitations, it is possible to deduce the kinetics. The mechanism of Claisen rearrangement suggests that a Langmuir–Hinshelwood–Hougen–Watson (LHHW) model can be used with chemisorption, surface reaction and desorption steps.

For a surface reaction controlled mechanism, the rate of reaction ($\text{mol}/\text{cm}^3 \text{ min}$) is given by

$$\begin{aligned} -r_A &= k'_{\text{SR}} C_{\text{AS}} = \frac{k'_{\text{SR}} K_A C_T C_A}{1 + K_A C_A + K_B C_B} \\ &= \frac{k_{\text{SR}} K_A w C_A}{1 + K_A C_A + K_B C_B} \end{aligned} \quad (1)$$

where A and B denote allyl-2,4-di-*tert*-butylphenyl ether and 6-allyl-2,4-di-*tert*-butylphenol, respectively, K_A and K_B the adsorption equilibrium constants for A and B, respectively (cm^3/mol), C_{AS} the concentration of adsorbed species A (mol/cm^3), k'_{SR} the reaction rate constant (min^{-1}), k_{SR} the reaction rate constant ($=\alpha k'_{\text{SR}}$) ($\text{cm}^3/\text{g-cat min}$), w the catalyst loading ($\text{g-cat}/\text{cm}^3$ liquid phase), C_T the total catalytic site concentration ($=\alpha w$) (mol/cm^3), α the constant of proportionality ($\text{mol}/\text{g-cat}$), and C_A and C_B are the bulk concentration of A and B, respectively (mol/cm^3).

Eq. (1) can be converted in terms of fractional conversion, X_A :

$$\begin{aligned} -r_A &= \frac{-dC_{A_0}}{dt} = C_{A_0} \frac{dX_A}{dt} \\ &= \frac{k_{\text{SR}} K_A w C_{A_0} (1 - X_A)}{1 + K_A C_{A_0} (1 - X_A) + K_B C_{A_0} X_A} \end{aligned} \quad (2)$$

$$-\ln(1 - X_A) + \frac{C_{A_0} X_A (K_A - K_B)}{1 + K_B C_{A_0}} = \frac{k_{\text{SR}} K_A w t}{1 + K_B C_{A_0}} \quad (3)$$

Eq. (3) can be manipulated to get:

$$-\frac{\ln(1 - X_A)}{X_A} = \left(\frac{k_{\text{SR}} K_A w}{1 + K_B C_{A_0}} \right) \frac{t}{X_A} + \frac{C_{A_0} (K_B - K_A)}{1 + K_B C_{A_0}} \quad (4)$$

Eq. (4) allows to extract the equilibrium constants and rate constant from the same data. Thus, by making the plot of left hand side term against t/X_A , the intercept and slopes could be obtained at different w values, to get all three constants. The above analysis was performed since there was a likelihood of strong adsorption of either reactant or product inhibiting the rate. The adsorption equilibrium constants for A and B can be compared to get three different cases as given below:

(a) If $K_A \gg K_B$

$$-\frac{\ln(1 - X_A)}{X_A} = (k_{\text{SR}} K_A w) \frac{t}{X_A} - C_{A_0} K_A \quad (5)$$

(b) If $K_A \ll K_B$

$$-\frac{\ln(1 - X_A)}{X_A} = \left(\frac{k_{\text{SR}} K_A w}{1 + K_B C_{A_0}} \right) \frac{t}{X_A} + \frac{C_{A_0} K_B}{1 + K_B C_{A_0}} \quad (6)$$

(c) If $K_A, K_B \ll 1$

$$-\ln(1 - X_A) = k_{\text{SR}} K_A w t = k_1 w t \quad (7)$$

It was observed that when plots of LHS term in Eqs. (5)–(7) were made against the term on RHS involving t , only Eq. (7) was found to hold, thereby suggesting very weak adsorption of A and B, leading to a first-order equation. Thus, a plot of $-\ln(1 - X_A)$ against time is shown in Fig. 7. It is seen that the data fit very well and thus validates the model that the reaction is intrinsically kinetically controlled by the surface reaction on the catalytic site, with weak adsorption of the reactant and product. An Arrhenius plot of $\ln k_1$ versus $1/T$ (Fig. 8) was used to calculate the values of the frequency factor k_0 and the energy of activation as $1.34 \times 10^5 \text{ cm}^3/\text{g-cat min}$ and 10.5 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 the active sites.

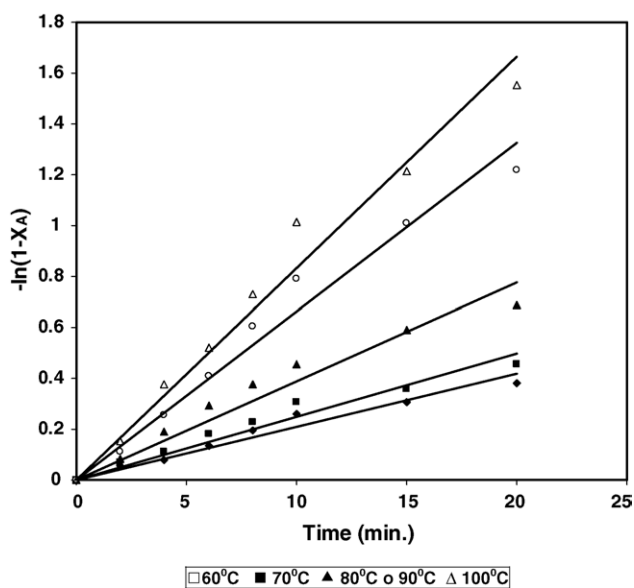


Fig. 7. First-order kinetic plot of Claisen rearrangement of allyl-2,4-di-*tert*-butylphenyl ether.

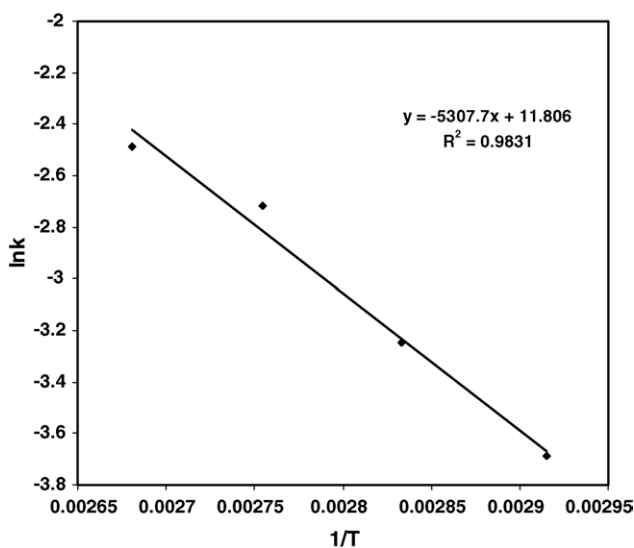


Fig. 8. Arrhenius plot.

4. Conclusion

Supported HPAs have become popular because of their redox nature, super acidic properties and the Keggin structure. They function ubiquitously in homogeneous as well as heterogeneous catalytic reactions. The Claisen rearrangement of allyl-2,4-di-*tert*-butylphenyl ether was successfully studied by using environmentally friendly several solid acid catalysts such as 20% w/w DTP/HMS, 20% w/w DTP/K-10, K-10, and sulphated zirconia. The activity of 20% w/w DTP/HMS was found to be superior to others. The effects of various parameters were studied on the rate of reaction under otherwise similar conditions. External mass-transfer

resistance was eliminated by providing adequate stirring and internal diffusion resistance was also absent due to mesoporosity and smaller particle size. It was observed that the catalyst has excellent reusability and the reaction was 100% selective towards allyl-2,4-di-*tert*-butylphenyl ether. A first-order kinetic model was developed to analyse the experimental data and the apparent activation energy is 10.5 kcal/mol, which also suggested that the reaction is intrinsically kinetically controlled.

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