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Cesium-substituted dodecatungstophosphoric acid on K-10 clay for benzoylation of anisole with benzoyl chloride

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Abstract

Synthesis of cesium-substituted dodecatungstophosphoric acid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) supported on K-10 clay is reported. The catalyst is fully characterized. It serves as a promising catalyst for the acylation of aromatic compounds. The acylation of anisole with benzoyl chloride was studied systematically by using 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 and this catalyst can be reused without any further chemical treatment, eliminating the effluent disposal problem. This acylation reaction is 100% selective toward 4-methoxybenzophenone, which is the desired perfumery intermediate. The effect of various important kinetic parameters was evaluated systematically to establish that the reaction obeys the Eley–Rideal type of mechanism with a very weak adsorption of the reactants. The reaction is free from any external mass transfer as well as intraparticle diffusion limitations and is intrinsically kinetically controlled.

Keywords: Cs-substituted dodecatungstophosphoric acid; Clay; Heterogeneous catalysis; Anisole; Benzoylation; 4-Methoxybenzophenone; Kinetics

1. Introduction

Functionalized aromatic ketones, produced via acylations, are of great importance in a variety of industries. For example, acylation of anisole (4-methoxybenzene) with benzoyl chloride or benzoic anhydride gives 4-benzoylanisole (4-methoxybenzophenone), which is a valuable perfumery intermediate and also a precursor for antioxidants used in cosmetics, PVC, unsaturated polyesters, acrylics, rubber, alkylated resins, cellulose lacquers, and oil paints. The most common method of introducing an acyl group into an organic compound is via the Friedel–Crafts reaction by using either aluminium chloride in nitrobenzene or boron trifluoride in liquid HF as a catalyst [1,2]. Various other Lewis acids such as $FeCl_3$, $ZnCl_2$, $SnCl_2$, $InCl_3$, $SbCl_5$, metal triflates, and Bronsted acids such as H_2SO_4 and HCl have been studied extensively [3] and all these lead to serious effluent problems on an industrial scale. Demand for a cleaner environment has attracted considerable attention to replace these homogeneous, polluting, and corrosive systems with environmentally benign heterogeneous acid catalysts. Zeolites have emerged as an alternative for the traditional polluting catalysts, but unfortunately the slow diffusion of reactants through their microporous structure makes them relatively poor catalysts in liquid phase reactions and their stability is susceptible in reactions where acids are generated as co-products. The use of highly reactive carboxylic acid halogenide compounds as acylating agents, as well as anhydrous HCl, which is produced during the reaction, may remove the aluminum species from the zeolite framework. Of late, several researchers have focused their attention on Hβ and HY zeolites for acylation of substituted aromatics including anisole. However, zeolites have been found to deactivate [4–9]. Thus, there is still a scope for developing better catalysts for acylation. The current work is a step in that direction.

Among many other solid acid systems, heteropoly acids (HPA) having Keggin anion structures have received the most attention due to their simple preparation and strong acidity [10,11]. Especially dodecatungstophosphoric acid (DTP) is the most extensively studied [12–14] since it possesses superacidity [15]. However, some of the major problems associated with HPAs in the bulk form are their low efficiency due to low surface area, rapid deactivation, and relatively poor stability. Attempts to improve the efficiency and stability of HPAs have been made by using various supports

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including mesoporous silica [16], mesoporous aluminosilicates [17], alumina and carbon [18,19], and zirconia [20]. Because of their basic nature, alumina and zirconia tend to decompose HPAs, resulting in deformation of the parent Keggin structure, thereby reducing the overall activity [20]. In this context, we had brought out the novelty of K-10 as a suitable support for HPAs, in a variety of industrially important reactions [21–27]. When HPAs are supported on K-10, no defects in the primary Keggin structure of HPAs were observed due to the acidic character of K-10 clay. Another method that enhances the HPA stability and activity in liquid phase reactions is to prepare catalysts in the form of alkali metal salts of HPA. Especially Cs salts of DTP have been reported to be better catalysts than DTP itself, but the particles of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ are very fine and separation of the catalyst from the liquid remains a problem. Direct impregnation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is not possible due to its insolubility in any kind of solvent [28,29].

The primary objective of our current work revolves around the synthesis of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported on K-10 clay (20% w/w) with intact Keggin anion. Benzoylation of anisole with benzoyl chloride was used as a model reaction to evaluate the reactivity and stability of this catalyst, where corrosive acid such as HCl is evolved as a co-product along with the desired aromatic ketone. This reaction is itself useful for studying the robustness of the catalyst and its reusability. The activity of the above-synthesized catalyst was also compared with other clay-based catalysts (possessing Bronsted and Lewis acidity) such as K-10 clay, 20% w/w dodecatungstophoshoric acid (DTP)/K10 and 20% w/w $ZnCl_2$/K-10, and sulfated zirconia.

2. Experimental

2.1. Chemicals

All the chemicals were A.R. grade and procured from reputed firms. Hexahydrate dodecatungstophosphoric acid (DTP), anisole, and $ZnCl_2$ were obtained from M/s s.d. Fine Chem. Ltd, Mumbai, India. Benzoyl chloride was procured from E-Merck India Ltd., Mumbai, India. Montmorillonite–K-10 was obtained from Fluka, Germany.

2.2. Preparation of catalysts

K-10 was dried at 120 °C for 3 h prior to its use. The following supported catalysts were prepared by well-developed procedures and characterized in our laboratory: 20% w/w $ZnCl_2$/K-10 [25] and 20% w/w DTP/K-10 [21–27] and sulphated zirconia [28,29].

$Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 (20% w/w) was prepared by the incipient wetness technique and calcined at 300 °C for 3 h. K-10 clay was first impregnated with aqueous solution of the Cs^+ precursor, dried at 110 °C for 12 h and calcined at 300 °C for 3 h. Following this, DTP was impregnated using a methanolic solution, dried at 110 °C for 12 h and calcined at 300 °C for 3 h. For comparison, bulk $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was prepared by adding the Cs precursor solution dropwise to the DTP solution while stirring. The resulting precipitate was dried at 110 °C for 12 h, and calcined at 300 °C for 3 h. All catalysts were powdered and dried at 120 °C for 3 h prior to their use.

2.3. Characterization of catalysts

Primary Keggin structures of bulk as well as supported HPA catalysts were confirmed by FT-IR analysis. FT-IR studies of the catalysts were conducted by using a Bruker IFS-66 single-channel Fourier transform spectrophotometer. Thin wafers were prepared by mixing 3 mg of catalyst with 100 mg of spectroscopic-grade KBr. The wafers were subjected to 200 scans, after which the spectra were recorded.

Crystallinity and textural patterns of the catalysts were predicted from XRD data, which were recorded using a Philips PW 1729 powder diffractometer with Cu-K_α(1.54 Å) radiation.

The BET surface area, pore volume, and pore size distribution were determined from BJH and multipoint BET methods by using a Micromeritics ASAP-2010 surface area analyzer.

Particle size distribution of 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 was studied by using a Tracor Northern Image analyzer.

2.4. Reaction procedure

The reactor consisted of a flat-bottomed cylindrical glass vessel of 100-ml capacity equipped with four baffles, a turbine stirrer, and a condenser. The assembly was kept in a thermostatic oil bath at a known temperature and mechanically agitated with an electric motor. A typical reaction mixture consisted of 0.0397 mol of benzoyl chloride and 0.27 mol of anisole with 1.05 g of catalyst. The total volume of the reaction mixture was 35 ml and thus the catalyst loading was 0.03 g/cm^3 of the total volume of the reaction mixture. The reaction was carried out at 70 °C at a speed of agitation of 800 rpm. Samples were withdrawn periodically and HPLC analyses were performed. 100% conversion of benzoyl chloride was observed when the reaction was carried out at 110 °C for 4 h. Due to very high reaction rate, it was not feasible to study the kinetics of the reaction at a temperature of 110 °C. Therefore, various kinetic parameters affecting the reaction rate were evaluated at 70 °C. All the data collected were in an error domain of 2%.

2.5. Analysis

In periodically withdrawn samples, methanol was added in excess to convert the remaining benzoyl chloride to methyl benzoate and analyses were performed on HPLC (Model: Toscho, UV-8010) by using a Merck 50983 column

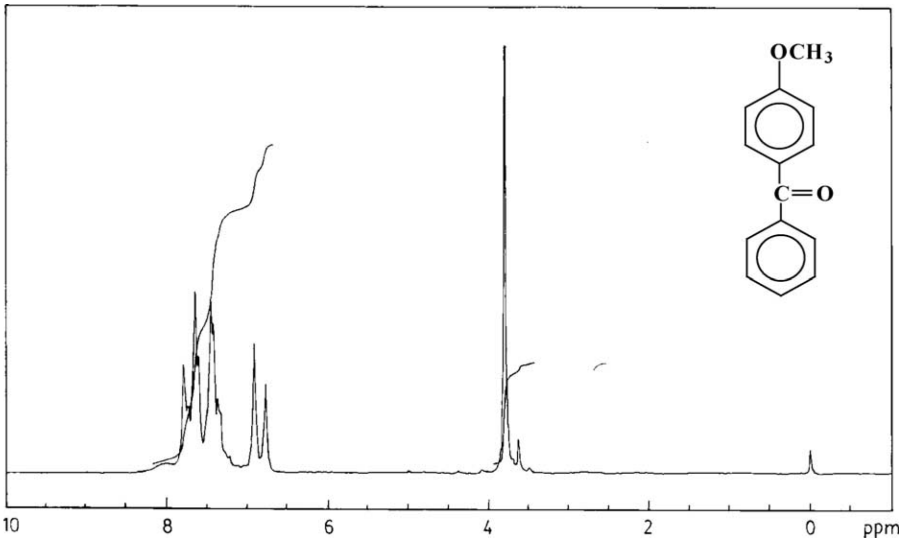


Fig. 1. ^{1}H NMR of 4-methoxybenzophenone.

with a stationary phase of Lichrospher 100 RP-18, particle size 5 µm, prepacked on a 250 mm × 4 mm i.d. column with a Tosoh UV-8010 detector set at 255 nm. The eluent used for analysis was 70:30 methanol (HPLC grade) and water at a flow rate of 0.8 ml min^{-1}. Quantitative results were obtained by comparing the results with the calibration from synthetic mixtures.

2.6. Identification and isolation of product

The reaction mixture was filtered to remove the solid catalyst and the product was isolated. Typically, the product was isolated from the reaction mixture after 3 h. The filtrate was treated with benzene and with water to remove traces of benzoyl chloride. Benzoic acid formed by the reaction of benzoyl chloride with water was removed by treating the mixture with $NaHCO_3$. The mixture was taken in a separating funnel and allowed to stand for few minutes, water was separated, the organic layer was taken in an evaporator to remove benzene and excess anisole, and the solid mass was then dissolved in methanol and tested with thin layer chromatography (TLC). Confirmation of the product was done through melting point, GC, and TLC by comparison with the standard product. The reaction was found to be 100% selective towards 4-methoxybenzophenone as confirmed by the above methods of analysis and by ^{1}H NMR (Fig. 1).

3. Results and discussion

3.1. Characterization

Complete characterization of K-10 [19], 20% w/w DTP/K-10 [21–27], sulphated zirconia [28,29], and 20% w/w $ZnCl_2$/K-10 [30–33] has been provided earlier in detail. Characterization of 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported on K-10 clay was done by employing the following techniques.

3.1.1. X-ray diffraction studies

Bulk DTP hexahydrate (Fig. 2a) is characterized by its cubic structure as shown in the XRD pattern presented in diffraction lines. It is found to be crystalline in nature. On the other hand, the crystallography structure is preserved while preparing $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ by exchanging the protons of bulk DTP with Cs^+ (Fig. 2b).

K-10 montmorillonite clay is an acid-treated montmorillonite (refluxed in an acid solution). The acids that are used to make K-10 by the treatment of its parent clay like Tonsil-13 (which has a ordered layer structure) are sulphuric acid, hydrochloric acid, and nitric acid. The parent clay is generally refluxed with one of these mineral acids at high temperature to produce K-10 montmorillonite. During the mineral acid treatment at high temperature, the lamellar structure (or typical montmorillonite structure) gets progressively destroyed. The XRD pattern in Fig. 2c is for delaminated K-10 montmorillonite, showing a peak of very low intensity at $2\theta = 9.8$, which may be due to the residual 2:1 (T–O–T) structure. The delamination during the process of preparation of K-10 results in an increase in surface area and formation of mesopores. In the case of K-10 there is observed a sharp peak at $2\theta = 26.2$, which belongs to the quartz and there is no effect on the 2θ value of quartz, even after exchanging the K-10 clay either with DTP (Fig. 2d) or with $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Fig. 2e). From the background XRD reflection in the K-10 sample, it is inferred that K-10 is amorphous in nature.

It was also observed that when DTP was impregnated on K-10 (Fig. 2d) and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ on K-10 (Fig. 2e), some crystallinity of DTP as well as $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was lost.

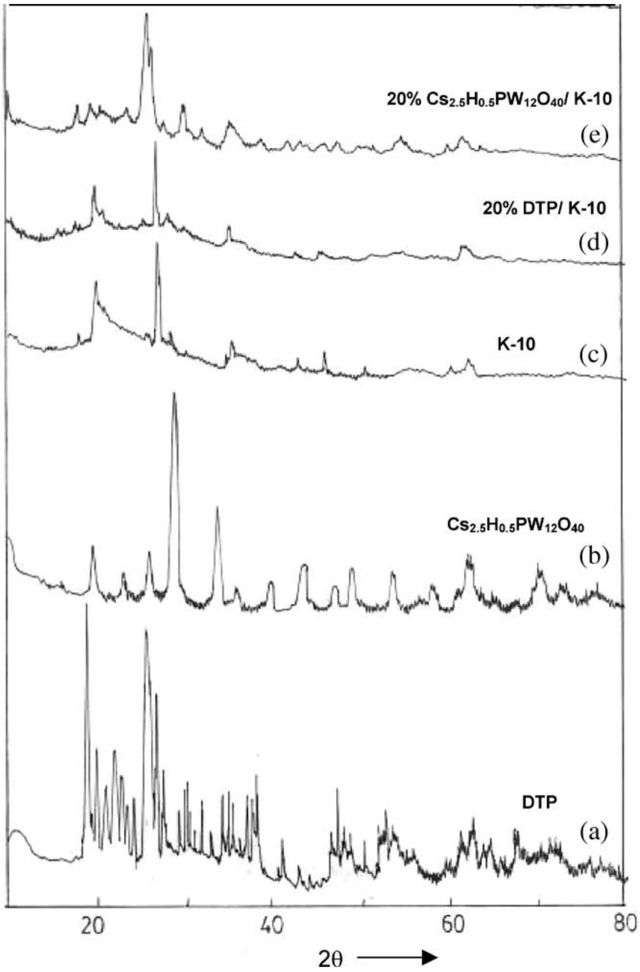


Fig. 2. XRD patterns.

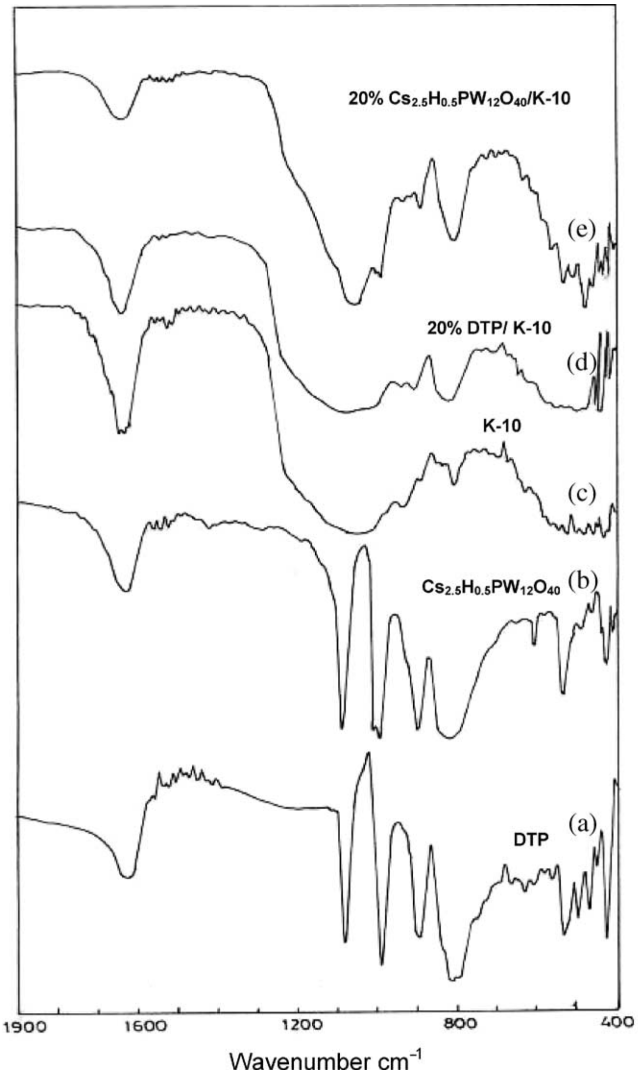


Fig. 3. FT-IR patterns.

3.1.2. *FT-IR*

The primary structure of supported HPAs (Proton form) as well as cesium salt of DTP were identified by comparing their FT-IR absorbance bands to those of bulk DTP, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, and K-10 clay (Fig. 3). Bulk DTP ($H_3PW_{12}O_{40}$) and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ show the characteristic IR bands at ca. 1080 cm^{-1} (P–O in central tetrahedral), 984 cm^{-1} (terminal W=O), and 897 and 812 cm^{-1} (W–O–W) associated with the asymmetric vibrations in the Keggin polyanion (Fig. 3a and 3b); however, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is characterized by a split in the W=O band, suggesting the existence of direct interaction between the polyanion and Cs^+. Similar observations have been observed for the case of W=O vibrations in $Cu_{1.5}PW_{12}O_{40}$ [34] and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported on mesoporous silica [35]. FT-IR of 20% w/w DTP/K-10 and 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 (Fig. 2d and 2e) indicate that the primary Keggin structure is preserved after supporting 20% w/w DTP and 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ on K-10. The bands in the region of 1600 to 1700 cm^{-1} (at 1631–1642 cm^{-1}) is attributed to an –OH bending frequency of water molecules present in catalysts (Fig. 3a–e). In DTP, it is present as water of crystallization (Fig. 3a), whereas in the case of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Fig. 3b), it indicates the presence of partial H^+ ion directly attached to the polyanion (–OH) and is present in K-10 as M–OH and possibly as H_3O^+ (Fig. 3c).

Furthermore, ^{31}P NMR analyses of 20% w/w DTP/K-10 and 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 show that there is a peak at a chemical shift of ca. −15 ppm with reference to 0 ppm response from 85% H_3PO_4 and it confirms that $[PW_{12}O_{40}]^{3-}$ was the only species present on the support. In particular no additional ^{31}P NMR peak, for example, at ca. −13 ppm, a peak generally attributed to a defect $(P_2W_{21}O_{71})^{-6}$ Keggin, was evident [36,37]. These results regarding a supported form of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ are in good agreement with those obtained by Choi et al. [35] for 50% $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported on mesoporous silica.

3.1.3. *Nitrogen adsorption*

It can be seen from Table 1 that the BET surface area of 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 is higher than that of 20% w/w DTP/K-10 and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and slightly

Table 1
Surface area, pore volume, and average pore diameter of catalysts used in the reaction

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)
K-10	230	0.36	64
20% DTP/K-10	107	0.32	71
20% $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10	207	0.29	58
Sulfated zirconia	100	0.115	28
20% w/w $ZnCl_2$/K-10	145	0.28	68

lower than that of K-10. The pore size distribution of sulphated zirconia suggests that the average pore sizes fall in the range of 35–50 Å with the maximum number of pores falling in the range of 38–45 Å [38], whereas for K-10 clay and K-10 clay based catalyst they are found to fall in the range of 50–75 Å suggesting that pore sizes of the catalysts lie in the mesoporous region, i.e., > 20 Å (Fig. 4). The adsorption–desorption isotherms for K-10, 20% DTP/K-10, 20% $ZnCl_2$/K-10, and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 show that they possess the type IV isotherm with the hysteresis loop of type H3, which is a characteristic of mesoporous solids.

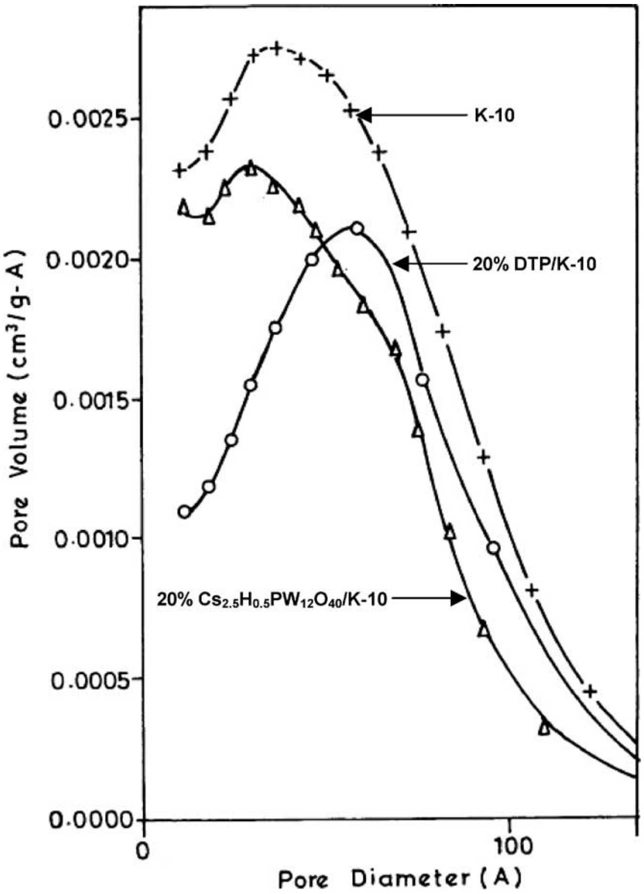
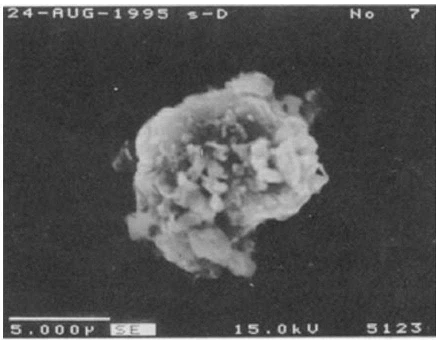


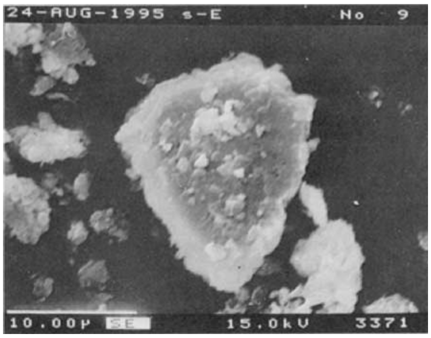
Fig. 4. Pore size distribution plots.

3.1.4. SEM analysis

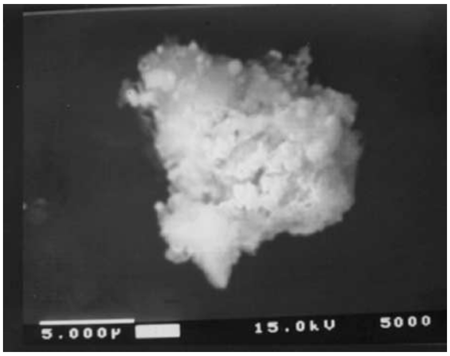
Figs. 5a, 5b and 5c show the scanning electron micrographs of K-10, 20% w/w DTP/K-10, and 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10, respectively. A distinct difference was visible among K-10, 20% w/w DTP/K-10, and 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10. It is clearly seen from the SEM micrographs that both K-10 and 20% w/w DTP/K-10 samples possess rough and rugged surfaces, whereas 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 shows a smoother surface due to a layer of (Cs salt of DTP) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ over the external surface of K-10. The catalysts K-10, 20% w/w DTP/K-10, and 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 have a particle size in the range of 5–10 µm.



(a) K-10



(b) 20% DTP/K-10



(c) 20% $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10

Fig. 5. SEM photographs

Table 2
Efficacies of various catalysts on conversion of benzoyl chloride and reaction rate

Catalyst	Initial activity (mol g-cat^{-1} s^{-1})	Conversion (%)
20% w/w $ZnCl_2$/K-10	16.6×10^{-4}	38
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 (20%)	10×10^{-4}	37
DTP (20%)/K-10	10×10^{-4}	32
S-ZrO_2	2×10^{-4}	26
K-10	1.66×10^{-4}	15

Benzoyl chloride:anisole = 1:7, catalyst loading = 0.03 g/cm^3, temperature = 70 °C, speed of agitation = 800 rpm, time = 2 h. DTP: dodecatungstophosphoric acid.

3.1.5. Particle size distribution

Since the newly synthesized catalyst is a K-10 clay based catalyst, it was decided to study the particle size distribution of 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10, although it was observed through its SEM micrograph that the catalyst particles are in the range of 5–10 µm. Particle size distribution analysis of 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 shows that the majority of the catalyst particles lie in the range of 2–10 µm.

3.2. Effects of catalysts

The efficacies of different catalysts at 70 °C are given in Table 2. The catalysts used were cesium ($Cs_{2.5}$) salt of dodecatungstophosphoric acid (DTP) supported on K-10 montmorillonite clay (20% w/w), 20% w/w DTP supported on K-10, 20% w/w $ZnCl_2$/K-10, sulphated zirconia, and K-10.

As observed from Table 2, 20% $ZnCl_2$/K-10 showed higher activity, for benzoylation of anisole followed by 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10, 20% w/w DTP/K-10, sulphated zirconia, and K-10. All the catalysts used were found to be 100% selective toward 4-methoxybenzophenone. No significant differences in final conversion of benzoyl chloride (after 2 h) were observed for 20% w/w $ZnCl_2$/K-10, 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10, and 20% w/w DTP/K-10.

It is generally believed that acylation of anisole with benzoyl chloride is a fairly easy reaction and even can take place in the absence of a catalyst. Therefore, it was decided to perform the reaction without catalyst and a standard reaction between 0.27 mol of anisole and 0.0397 mol of benzoyl chloride (as mentioned earlier) was carried out at 70 and 110 °C and reflux temperature for 4 h. These temperatures were decided in consonance with the temperature range selected in the current study. On analysis, the resultant reaction mixture (after 4 h) showed that no benzophenone derivative was formed. These results confirmed that the reaction does not take place in the absence of catalyst.

3.3. Reusability and stability of the catalyst

The stability of the active species in solution has been of concern for solid acids, especially for supported materials. Since 20% w/w $ZnCl_2$/K-10, 20% w/w DTP/K-10, and 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 showed comparable results, to select the best candidate catalyst on its stability, their reusability studies were performed. High activity of $ZnCl_2$ supported on K-10 is due to a high local concentration of Zn^{2+}. However, the reusability of this catalyst was found to be unfavorable. Clark's group has reported that some of the active sites of 20% w/w $ZnCl_2$/K-10 become poisoned by an oxygenated substrate (aromatic ethers, such as anisole, poison the catalyst active sites in liquid phase reactions) or product molecules, resulting in a substantial loss of efficiency of the catalyst during its reusability. As mentioned earlier, the potential use of HPAs supported on K-10 clay has been well explored by Yadav et al. in a variety of reactions including alkylation, etherification, and dehydration [21–27]. 20% w/w DTP/K-10 has been found to work efficiently for acylation reactions (when acetyl chloride is used as an acylating agent) in the liquid phase [39], but when the above catalyst is used in the acylation reactions involving a highly corrosive acylating agent such as benzoyl chloride [40], efficiency of the catalyst decreases. To establish the effect of reusability in the presence of benzoyl chloride, reusability of 20% w/w DTP/K-10 and 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 was studied three times, including the use of fresh catalyst, and is shown in Fig. 6. After first use and before every reuse, the catalysts were washed with methanol and recalcined at 300 °C for 3 h to remove the adsorbed reactants and product. When 20% w/w DTP/K-10 was used, a decrease in conversion was observed with its subsequent reuse, while on the other hand when 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 was repeatedly used, no significant effect was observed, although a minor decrease in final conversions was observed. A decrease in catalytic activity of 20% w/w DTP/K-10 due to the deteriorating condition of DTP and its subsequent leaching from the support into the liquid phase which was confirmed by the leaching test as well [24]. This was further confirmed by a UV spectrum test of supernatant portions of 20% w/w DTP/K-10 and 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 catalyzed reaction mixtures. When a supernatant portion of DTP/K-10 catalyzed reaction mixture was subjected to the UV spectrum, it exhibited an adsorption band at around 265 nm assigned to Keggin-type $PW_{12}O_{40}{}^{-3}$ ions [41], whereas in the case of 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 no such band was visible at 265 nm. The stability of 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 was also confirmed by FT-IR spectra of fresh and used 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10. No change in primary Keggin anion was observed for used 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10, even after its repeated use in the presence of benzoyl chloride, which could have led to deformation in its primary Keggin structure. In addition to

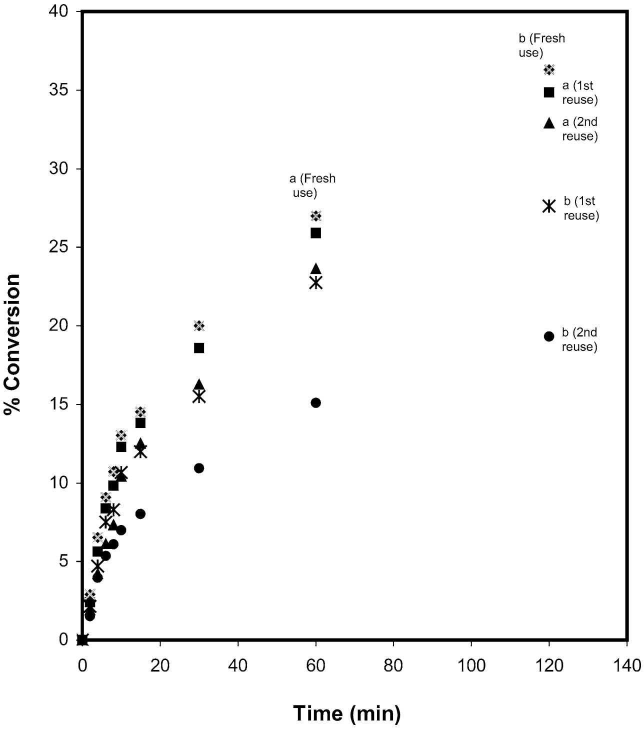


Fig. 6. Effect of reusability on (a) $Cs_{2.5}H_{0.5}PW_{12}O_{40}/K\text{-}10$ (20%) and (b) DTP/K-10 (20% w/w). Benzoyl chloride:anisole = 1:7, catalyst loading = 0.03 g/cm^3, speed of agitation = 800 rpm, time = 2 h, temperature = 70 °C.

the UV test, when the supernatant portion of 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}/K\text{-}10$ catalyzed reaction was subjected to FT-IR to detect any leaching of active polyoxometalate species ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) from the K-10 clay, there was no leaching of active species at all as no IR spectra were observed in the range of 812–1080 cm^{-1} (characteristic bands of primary Keggin anion) as well as the whole inorganic range. These results clearly show that 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}/K\text{-}10$ is very stable in the presence of corrosive and strong acylating agents such as benzoyl chloride and this has been further confirmed by study of heterogeneity of the reaction system by employing 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}/K\text{-}10$ as a catalyst.

3.4. *Heterogeneity of the reaction system*

To further bolster the inferences drawn on the stability of catalyst and about the intactness of active species ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) with K-10 clay (support), the reaction mixture was filtered after 2 h (reaction was conducted at the standard condition) and the reaction with filtrate, in the absence of any external added catalyst, was further continued, under otherwise similar conditions. No increase in conversion was observed, even after 6 h. An increase in conversion would have taken place had there had been any presence of leached active species in the filtrate of reaction mixture. This fact confirms that newly prepared 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}/K\text{-}10$ is very stable and active species do not get leached out of the K-10 (support) and reaction does not take place in the absence of catalyst.

Therefore, in all further reactions 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}/K\text{-}10$ was used as a catalyst, which not only exhibits the high activity but also shows the catalyst is reusable.

3.5. *Proof of absence of external mass transfer resistance*

To assess the role of external mass transfer on the reaction rate, the effect of the speed of agitation was studied. The speed of agitation was varied from 800 to 1500 rpm. It was observed that the conversion of benzoyl chloride was practically the same in all the cases. Thus, it was ensured that external mass transfer effects did not influence the reaction. Hence, all further reactions were carried out at 800 rpm. A theoretical analysis of the assessment of external mass transfer resistance is given to support this observation. Details of this theory for general slurry reactions are given elsewhere [29].

This reaction is a typical solid–liquid slurry reaction involving the transfer of benzoyl chloride, the limiting reactant (A), and anisole (B) from the bulk liquid phase to the catalyst wherein external mass transfer of reactants to the surface of the catalyst particle, followed by intraparticle diffusion, adsorption, surface reactions, and desorption, take place. The influence of external solid–liquid mass transfer resistance must be ascertained before a true kinetic model could be developed. Depending on the relative magnitudes of external resistance to mass transfer and reaction rates, different controlling mechanisms have been put forward [42]. The liquid phase diffusivity values of the reactants A (benzoyl chloride) and B (anisole), denoted by D_{AB} and D_{BA}, were calculated by using the Wilke–Chang equation [43] at 70 °C as 2.57×10^{-5} and 2.88×10^{-5} cm^2/s, respectively. The solid–liquid mass transfer, coefficients for both A and B were calculated from the limiting value of the Sherwood number (e.g.), $Sh_A = k_{SL\text{-}A} d_p / D_{AB}$ of 2. The actual Sherwood numbers are typically higher by order of magnitude in well-agitated systems, but for conservative estimations a value of 2 is taken [29,44]. The solid–liquid mass transfer coefficients $k_{SL\text{-}A}$ and $k_{SL\text{-}B}$ values were obtained as 5.14×10^{-2} and 5.76×10^{-2} cm/s, respectively. The initial rate of reaction was calculated from the conversion profiles.

3.6. *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 liquid phase volume. The catalyst loading was varied over a range of 0.005–0.03 g/cm^3 on the basis of total volume of the reaction mixture. Fig. 7 shows the effect of catalyst loading on the conversion of benzoyl chloride. The conversion increases with increasing catalyst loading, which is due to the proportional increase in the number of

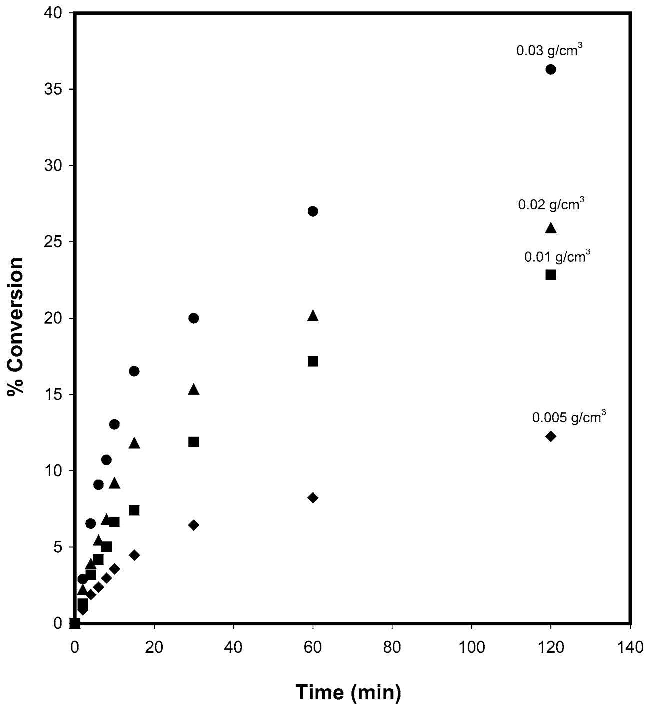


Fig. 7. Effect of catalyst loading. Benzoyl chloride:anisole = 1:7, catalyst = $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 (20%), speed of agitation = 800 rpm, temperature = 70 °C, time = 2 h.

active sites. Therefore, all further experiments were carried out at 0.03 g/cm^3 of catalyst loading.

At steady state, the rate of external mass transfer (i.e., from the bulk liquid phase in which A and B are located with concentration $[A_0]$ and $[B_0]$, respectively) to the exterior surface 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 of liquid volume. It is possible to calculate the values of $[A_S]$ and $[B_S]$. For instance,

$$k_{SL-A}a_P\{[A_0]-[A_S]\} = r_{obs} \text{ at steady state} \\ = 3\times10^{-5}\ \text{mol}\,\text{cm}^{-3}\,\text{s}^{-1}. \qquad (1)$$

From the calculations, it was observed that $[A_S] \approx [A_0]$; similarly $[B_S] \approx [B_0]$. Thus, any further addition of catalyst is not going to be of any consequence for external mass transfer.

3.7. Proof of absence of intraparticle resistance

Since the average particle size of 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 was found to be in the range of 2–10 µm and the catalyst is amorphous in nature, it was not possible to study the effect of catalyst particle size on the rate of reaction. The average particle diameter of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 used in the reactions was 0.001 cm (as analysed from particle size distribution data) and thus a theoretical calculation was done based on the Wiesz–Prater criterion to assess the influence of intraparticle diffusion resistance [43].

According to the Wiesz–Prater criterion, the dimensionless parameter 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), effective diffusivity of the limiting reactant (D_e), and concentration of the reactant at the external surface of the particle.

(i) If $C_{wp} = -r_{obs}\rho_p R_p^2/D_e[A_s] \gg 1$, then the reaction is limited by severe internal diffusional resistance.
(ii) If $C_{wp} \ll 1$, then the reaction is intrinsically kinetically controlled.

The effective diffusivity of benzoyl chloride (D_{e-A}) inside the pores of the catalyst was obtained from the bulk diffusivity (D_{AB}), porosity (ε), and tortuosity (τ) as $3.25\times10^{-6}\ cm^2/s$ where $D_{e-A} = D_{AB}\cdot\varepsilon/\tau$. In the present case, the value of C_{wp} was calculated as 1.818×10^{-3} for the initial observed rate, which is much less than 1, and this signifies the absence of resistance due to intraparticle diffusion; therefore, the reaction could be considered as an intrinsically kinetically controlled reaction. Further proof of the absence of intraparticle diffusion resistance was obtained through the study of the effect of temperature and it will be evaluated later.

3.8. Effect of mole ratio

The effect of mole ratio was studied at an anisole to benzoyl chloride ratio of 1:1 to 7:1 (Fig. 8) under otherwise similar conditions. As the concentration of anisole is increased w.r.t. the concentration of benzoyl chloride, an increase in conversion of benzoyl chloride and the rate of reaction is observed, which is quite evident from the graphs for a mole ratio of 3:1 to 7:1. This is because at the lower concentration of benzoyl chloride more active sites of catalyst are available for its surface adsorption, which results in quantitatively large formation of active electrophilic benzoylinium cation to react with anisole. At lower mole ratios, the concentration of bezoyl chloride w.r.t. anisole increases and the active sites become saturated with benzoyl chloride, resulting in quantitatively low formation of active electrophilic benzoylinium to react with anisole present in the bulk phase, thereby showing a decrease in conversion of benzoyl chloride and rate of reaction. Therefore, all the subsequent reactions were carried out with a mole ratio of 7:1 without any solvent, where anisole used in excess acts as a solvent.

3.9. Effect of temperature

The effect of temperature was studied from 50 to 110 °C (Fig. 9). The conversion was found to increase substantially

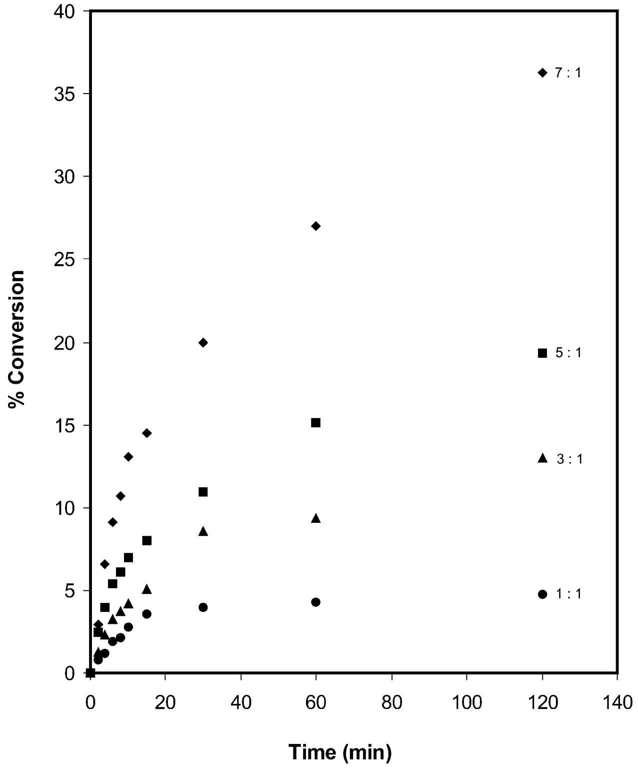


Fig. 8. Effect of mole ratio. Benzoyl chloride:anisole, catalyst = $Cs_{2.5}H_{0.5}PW_{12}O_{40}/K\text{-}10$ (20%), catalyst loading = 0.03 g/cm^3, temperature = 70 °C, speed of agitation = 800 rpm, time = 2 h.

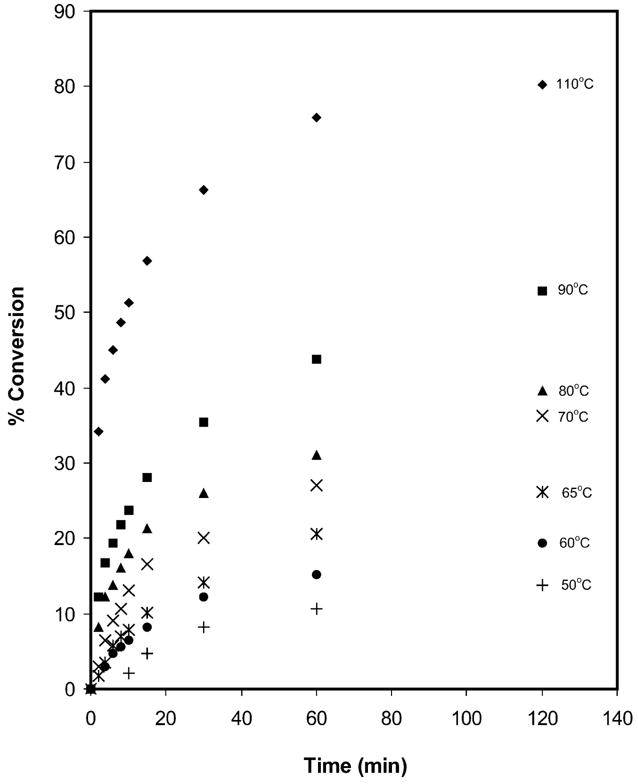


Fig. 9. Effect of temperature. Benzoyl chloride:anisole = 1:7, catalyst = $Cs_{2.5}H_{0.5}PW_{12}O_{40}/K\text{-}10$ (20%), catalyst loading = 0.03 g/cm^3, speed of agitation = 800 rpm, time = 2 h.

with increasing temperature, which suggested that the reaction was intrinsically kinetically controlled. The value of activation energy (Section 3.11) 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.

3.10. Reaction mechanism and kinetics

From the calculated values of mass transfer rates of A and B, initial observed rate, it is evident that the rate is independent of the external mass transfer effects. It is also seen from the values of activation energy that the intraparticle diffusion resistance is absent. Thus, the reaction could be controlled by one of the following steps, namely, (a) adsorption (b) surface reaction, or (c) desorption. Therefore, further development of the actual reaction mechanism was undertaken.

3.11. Development of mechanistic model

The adsorption studies of anisole and benzoyl chloride were performed to predict the actual mechanism of reaction. The adsorption constants calculated for benzoyl chloride (K_B) and anisole (K_A) were found to be 859 and 50 cm^3/mol. Although it seems from the adsorption studies that adsorption of anisole takes place up to some extent but it is quite negligible in comparison with that of benzoyl chloride, indicating that $K_B \gg K_A$.

Based on the preliminary studies, a reaction mechanism involving $Cs_{2.5}H_{0.5}PW_{12}O_{40}/K\text{-}10$ as a catalyst was proposed (Fig. 10) and validated. Other models such as Langmuir–Hinshelwood–Hougen–Watson and power law were also tested. For the catalytic activity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}/K\text{-}10$, the Eley–Rideal model was found to hold. The reaction involves two organic phase reactants, A (anisole), B (benzoyl chloride), the desired product C (4-methoxybenzophenone), and D (co-product HCl). The Eley–Rideal mechanism has already been found to be valid for our earlier work of acylation of mesitylene with acyl chloride [39] and acylation of 2-methoxynaphthalene with acetic anhydride [45], where adsorption of only acylating agents has been considered, because the formation of acylinum ion is very important in the reaction.

The first step involves the formation of carbocation by the adsorption of benzoyl chloride on a catalytic site (S):

$$\underset{(B)}{C_6H_5COCl} + \underset{(S)}{H^+} \underset{k'_B}{\overset{k_B}{\rightleftarrows}} \underset{(BS)}{C_6H_5CO^+} + \underset{(D)}{HCl\uparrow}. \tag{2}$$

The rate of chemisorption of B:

$$-r_B = k_B C_B C_S - k'_B C_{BS} C_D, \tag{3}$$

$$-r_B = 0, \quad \text{at equilibrium (quasi-equilibrium)}$$

$$k_B C_B C_S = k'_B C_{BS} C_D, \tag{4}$$

$$C_{BS} = \frac{k_B C_B C_S}{k'_B C_D}. \tag{5}$$

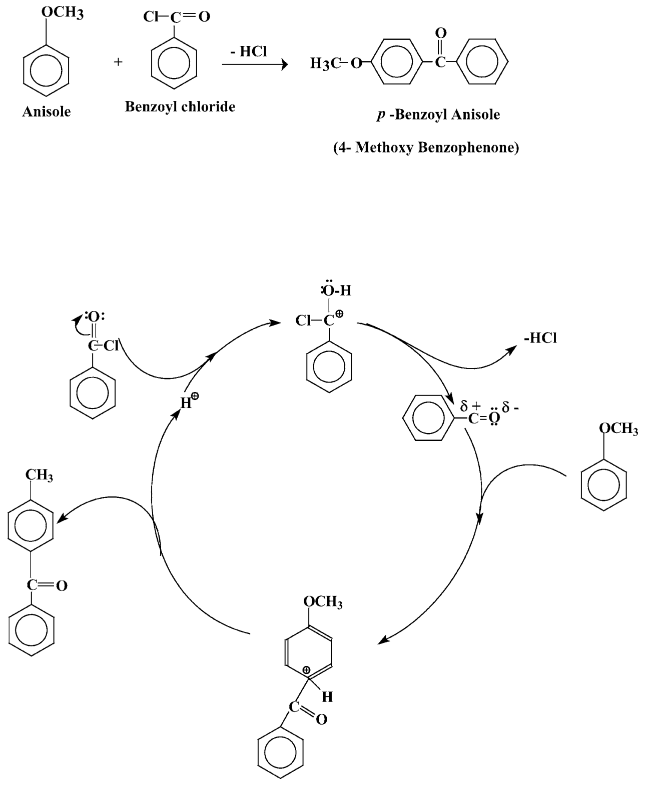
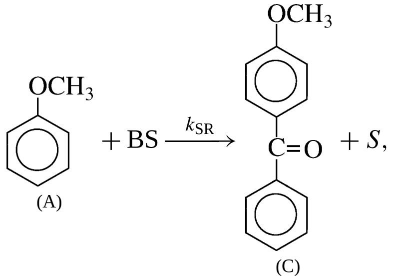


Fig. 10. Reaction mechanism.

Since $K_B = k_B/k'_B$

$$C_{BS} = K_B \frac{C_B C_S}{C_D}. \tag{6}$$

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



where k_{SR} = reaction rate constant.

The rate of reaction of benzoyl chloride per unit liquid volume is given by

$$-\frac{dC_B}{dt} = k_{SR} C_A C_{BS} = \text{rate of reaction of B}. \tag{7}$$

After substituting for C_{BS}

$$-\frac{dC_B}{dt} = k_{SR} C_A \frac{K_B C_B C_S}{C_D} = (k_{SR} K_B) \frac{C_B C_A C_S}{C_D}. \tag{8}$$

The total site balance is as follows,

$$C_{total} = w = C_{BS} + C_{AS} + C_S, \tag{9}$$

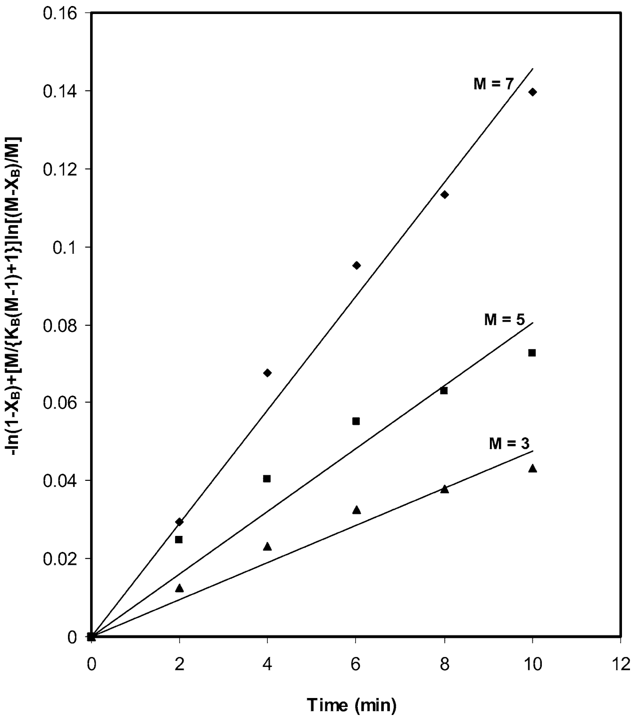


Fig. 11. Plot of $-\ln(1 - X_B) + [M/\{K_B(M-1)+1\}] \ln\{(M - X_B)/M\}$ vs time for different values of M.

where w is the catalyst loading. But $C_{AS} = 0$,

$$w = C_{BS} + C_S,$$

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

$$C_S = \left(\frac{w}{1 + \frac{K_B C_B}{C_D}}\right), \tag{10}$$

$$-\frac{dC_B}{dt} = k_{SR} C_A \frac{K_B C_B C_S}{C_D} = (k_{SR} K_B) \frac{C_B C_A}{C_D} \left(\frac{w}{1 + \frac{K_B C_B}{C_D}}\right), \tag{11}$$

$$-\frac{dC_B}{dt} = \frac{k_{SR} K_B w C_B C_A}{(C_D + K_B C_B)} = r_B,$$

$$C_B = C_{B_0}(1 - X_B),$$

$$C_A = C_{A_0} - C_{B_0} X_B = C_{B_0}(M - X_B),$$

$$C_D = C_{B_0} X_B. \tag{12}$$

Where, $C_{A_0}/C_{B_0} = M$, the initial mole ratio of anisole to benzoyl chloride, substituting in terms of X_B, the fractional conversion of B, and integrating, the following equations are obtained.

Case a $(M \neq 1)$.

$$-\ln(1 - X_B) + \left[\frac{M}{K_B(M-1)+1}\right] \ln\left[\frac{M - X_B}{M}\right] = \left[\frac{k_{SR} K_B (M-1) w t}{K_B(M-1)+1}\right]; \tag{13}$$

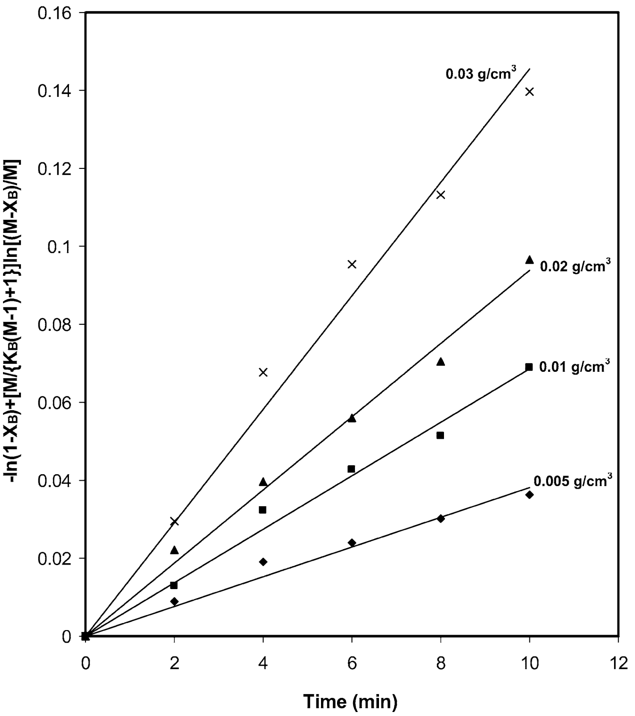


Fig. 12. Plot of $-\ln(1-X_{\mathrm{B}})+[M/\{K_{\mathrm{B}}(M-1)+1\}]\ln\{(M-X_{\mathrm{B}})/M\}$ vs time at different catalyst loading.

Case b ($M=1$).

$$\ln(1-X_{\mathrm{B}})+\frac{1}{(1-K_{\mathrm{B}})}\frac{X_{\mathrm{B}}}{(1-X_{\mathrm{B}})}=\frac{k_{\mathrm{SR}}K_{\mathrm{B}}wt}{(1-K_{\mathrm{B}})}. \tag{14}$$

The various equations were validated against the experimental data to establish the validity of Eq. (13) for $M \neq 1$ (Fig. 11) wherein $K_{\mathrm{B}} = 859\ \mathrm{cm}^3/\mathrm{gmol}$. In the same way, Eq. (14) was also validated for $M = 1$. It would therefore mean that the reaction mechanism is of the Eley–Rideal type of mechanisms in the absence of any diffusion resistance.

Fig. 12 shows four straight lines passing through the origin at catalyst loadings of 0.5, 1, 2, and 3% w/v, respectively. The slopes of these lines are

$$k=\frac{k_{\mathrm{SR}}K_{\mathrm{B}}(M-1)w}{K_{\mathrm{B}}(M-1)+1},$$

which are functions of w for the same molar ratio M, indicating that the rate is proportional to the number of active sites present on the surface. Therefore, by putting the value of K_{B} in the above equation, the values of k_{SR} could be found and activation energy was calculated from the plot of $\ln k_{\mathrm{SR}}$ vs $1/T$ as 15.6 kcal/mol (Fig. 13). This value also suggests that the reaction is kinetically controlled.

4. Conclusion

The synthesis of $\mathrm{Cs_{2.5}H_{0.5}PW_{12}O_{40}}$ (20% w/w) supported on K-10 clay has been reported and $\mathrm{Cs_{2.5}H_{0.5}PW_{12}O_{40}}$ was successfully impregnated onto K-10 clay with complete intact Keggin anion structure. This catalyst has been found to exhibit excellent activity for benzoylation of anisole. Amongst various catalysts used in this reaction 20% w/w $\mathrm{Cs_{2.5}H_{0.5}PW_{12}O_{40}}$/K-10 was found to be a better catalyst. Various kinetic parameters were studied for benzoylation of anisole over 20% w/w $\mathrm{Cs_{2.5}H_{0.5}PW_{12}O_{40}}$/K-10. The reaction follows the second-order kinetics and it was found to be intrinsically kinetically controlled. The catalyst was found to exhibit 100% selectivity toward 4-methoxybenzophenone. The studies were conducted 3 times including its fresh use and the catalyst showed excellent reusability; no change in its primary Keggin anion was observed, even after its repeated use in the reaction.

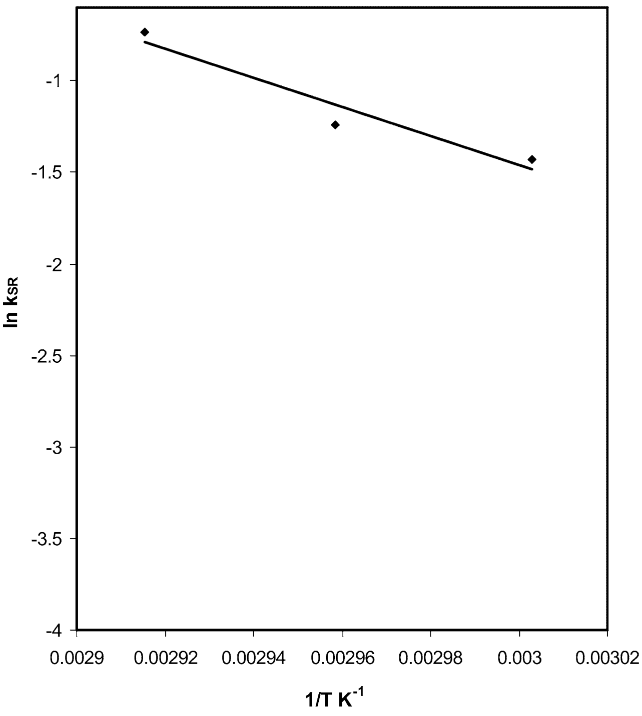


Fig. 13. Arrhenius plot. (Plot of $\ln k_{\mathrm{SR}}$ vs $1/T$). Benzoyl chloride:anisole = 1:7, catalyst = $\mathrm{Cs_{2.5}H_{0.5}PW_{12}O_{40}}$/K-10 (20%), catalyst loading = 0.03 g/cm^3, speed of agitation = 800 rpm, time = 2 h.

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