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Heterogeneous polymer supported and soluble tantalum metal complex catalysts for acylation reaction: A kinetic study

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New soluble and insoluble Tantalum pentachloride complex catalysts are prepared by simple procedures using pyridine and polymer-supported cross-linked (poly-4-vinyl pyridine) beads (PSCPVP) respectively as supports and Tantalum pentachloride as a catalytic moiety ($TaCl_5$). The prepared soluble Py-$TaCl_5$ and insoluble bead-shaped PSCPVP-$TaCl_5$ catalysts have been characterized with FT-IR, UV-Vis, SEM, TGA and elemental analysis techniques. The catalytic efficiency of these catalysts has been examined through acylation of ethanol as a model reaction under identical pseudo first order reaction condition. From the calculated k_{obs} values, it has been noticed that both the catalysts are active and however, Py-$TaCl_5$shown 1.65 fold has increased activity (k_{obs} =11.42x10^3 min^{-1}) than insoluble PSCPVP-$TaCl_5$ catalyst ($k_{obs=}$ 6.98x$10^{3,}$ min^{-1}). Although, PSCPVP-$TaCl_5$ has shown lesser activity than soluble due to its lower cost, recyclability and reusable nature up to third cycle, it has received greater recognition. Hence, in order to utilize this insoluble bead-shaped PSCPVP-$TaCl_5$ catalyst to pack in column reactor and to carry out the same reaction for continuous mode operation at industrial level, detailed kinetics study for acylation of ethanol has been conducted under pseudo first order condition by varying the different experimental parameters and has observed that each parameter has influenced the reaction. The obtained k_{obs} value reveals that reaction rates increase with the increase in the stirring speed, [substrate], [catalyst] and temperature. The thermodynamic parameters viz., activation energy (E_a), entropy ($\Delta S^{\#}$), enthalpy ($\Delta H^{\#}$) and free energy ($\Delta G^{\#}$) for the reaction are also calculated for the first time and their observed values are 35.2 kJmol^{-1}, -64.6 kJ^{-1}mol^{-1}, 37.7 kJmol^{-1}and 57.3 kJmol^{-1} respectively. The prepared insoluble catalyst is stable even after its use for three times in acylation without losing its efficiency, thus it is better suited for industrial applications.

Keywords: Acylation, Lewis Acid Catalyst, Metal containing polymers, Supported transition metal catalyst, Tantalum Pentachloride Complex

Development of novel catalysts for selective and effective organic transformations is an important step in organic synthesis. Homogeneous catalysts have been frequently used to conduct organic reactions due to their high activity and selectivity even under mild **reaction** conditions. But, because of the difficulty in their recovery, their commercial utility for organic synthesis has not been fully realized. Further, it is also proved that the cost of production and the amount of pollution that arises in homogeneously catalyzed reactions are relatively very high. In this context, the heterogeneous catalysts are convenient alternatives to homogeneous catalysts for organic reactions[1,2]. As a result, factors like expenditure and pollution are considerably reduced owing to the easy reusability, longevity and environmentally benign nature of the heterogeneous catalysts. Further, the heterogeneous catalysts may also be used in liquid-solid and gas-solid contact reactors. Because of these salient features of the heterogeneous catalysts, their commercial application in industries has been significantly increased. In fact, the interests in research on the development of new heterogeneous catalysts have been increasing year after year**.** Normally, heterogeneous catalysts are prepared by immobilization or anchoring of the active moiety on the inorganic/polymeric support. Insoluble bead-shaped polymer-supported catalysts are industrially important materials because of their easy handling and reusability via simple filtration. The immobilization of catalytically active metal on organic polymer matrices has been considered a greener catalytic route to carry out organic reactions in single/biphase medium particularly for esterification.

Lewis acid catalyzed organic reactions particularly "esterification" are considered to be a safer and potential method of current interest[3]. More particularly, for acylation of alcohols, many acid and base acetylation reactions have limited applications[4,5]. However, esterification of alcohol conversion has an essential synthetic transformation. Development of new Lewis acid catalyst is an emerging research study to carry out the acylation reaction effectively. The detailed literature studies reveal that the transition metal based Lewis acid complex catalysts have been successfully employed to conduct the esterification reactions[3-6]. The soluble forms of Lewis acid such as $TiCl_4$, $ZrCl_4$ and $SnCl_4$ are found potentially useful for industrially important reactions viz., acylation, ketalization and esterification[7,8]. However, because of the lack of success in reusability and cost factors, the use of above soluble Lewis acid catalysts are on the decline in industry. With a view to tackle these problems, the insoluble Lewis acid catalysts obtained by immobilization of various soluble metal Lewis acid onto the inorganic/organic matrix like clay, zeolites and unshaped polymer matrix have been exploited. However, use of these metal insoluble supports has been on the decline due to problems like leaching, low efficiency, high cost, poor catalyst recycling, passivity and corrosion of metals.

The complexes obtained from pyridine or triethylamine with transition metal are proved to be good complex catalysts owing to their effective co-ordination and stability. Particularly $TiCl_4$, $ZrCl_4$, $SnCl_4$, and $SbCl_4$ metal complexes with pyridine in the form of polymer-supported insoluble and soluble catalysts have been used effectively to facilitate the esterification and other organic reactions[7,8]. But, we strongly believe that most of the reported Lewis acid complex/catalyst suffer from the following disadvantages: vigorous reaction conditions, long reaction time, unavailability of the reagents and the occurrence of side reactions, as well as very poor yield in the respective products. The catalytic reactivity has been depicted to the valance state and complex composition of the metals. The mole ratio is also practically calculated by complexes and by the diffusion reactants to active centres with the polymer supported metal complexes. The kinetic study of esterification and acylation with *n*-butanol using PVP-$TiCl_4$ has been reported by Balakrishnan *et al.*[9]

The Lewis acids are well known acid catalysts which are frequently used to improve the yield in organic transformations. In general, if Lewis acids are derived from metal complex, their high catalytic activity is due to the nature of metallic sites, the complexed halogen and their structures. For example, the heavier group of 15 trihalides MX_3 in which M = Sb and As and X = Br and Cl are reported to be weak Lewis acids towards a variety of donor ligands. W. Leavson *et al.*, reported Lewis acid complex with poly and bi dentate and macrocylic and telluro-ether ligands[10-12]. Similarly, complexes of trihalides with R_3PO, R_3AsO, R_3PS and R_3PSe are reported, mostly of MX_3:2L stoichiometry. Further, Lewis acids such as $TaCl_5$, Me_3SiOTf, $Cu(OTf)_2$, $MgBr_2$, $Se(OTf)_3$ and other Lewis acid salts are also reported as catalysts for acylation of amines and alcohols with acid anhydrides[13-18]. It was also studied that majority of metal triflates are very expensive and water-sensitive. In fact, reagents like Me_3SiO_7 are very strongly acidic which is not to be used for the acid sensitive acylation of alcohols.

Polymer-supported Lewis acids are prepared by impregnation of acid halide or metals in a polymer or by interaction with the major functional group of resin[19-21]. The most frequently used resin for the preparation of supported Lewis acid catalysts is polystyrene. It prevents the hydrolysis of the complex until it is placed in a particular solvent. In addition, the presence of the polymer mediates the function of very strong Lewis acid catalyst and facilitates high yields of the desired products. Based on such features of polymer supported homogenous catalysts in the present study, it has been aimed to support Tantalum pentachloride on polyvinylpyridine to obtain the heterogeneous catalysts abbreviated as PSCPVP. The catalyst is used to catalyse the acylation of ethanol with acetic anhydride. The same reaction is also studied with soluble Py-$TaCl_5$ complex catalyst and the results are compared under same experimental conditions.

Experimental Section

Styrene (>99%, Fluka) and divinylbenzene (80%, Fluka) were used as received for the preparation of polymer beads. The monomer, 4-vinylpyridine (96%, Fluka) was distilled under pressure and used for the preparation. AIBN (98%, Koch-light) was recrystallized from ethanol. Gelatin (100%, BDH), boric acid (99.9%, Merck), polyvinyl alcohol (99%, Fluka), NaOH (98%, SRL), $NaNO_2$ (99%, SRL), $TaCl_5$ (99.9%, Alfa Aesar), acetic anhydride (99%, Thomas Baker) have been used as such. Solvents like chloroform, methanol, acetone, ethanol and other organic reagents were received from Merck with 99.8% purity. All the chemicals were purchased from Indian Companies.

Characterization methods

The FT-IR spectrum was recorded on Bruker FT-IR spectrophotometer with OPUS software. The sample was prepared with grinding of KBr with required sample amount and pure KBr pellet was used for background calibrations. UV Vis spectra was measured using instrument of Techomp8500 instrument with UV-Vis analyst software in the wavelength range of 200 nm to 800 nm. CHN analysis was been conducted with Elementar Vario EL III CHN Analyzer. For SEM analysis, as trip of double sided conducting carbon tape has been applied to the metal stub and the samples viz., plain PSCPVP beads and polymer-supported metal complex catalysts, PSCPVP-$TaCl_5$ having mesh size of +80-100 has been deposited on the carbon tape. The polymer supported catalysts were made conducting with gold coating through auto fine-coating ion sputter method and the SEM images were recorded using HITACHIS-3000H microscope. The thermo gravimetric analysis was carried out with ZETSCH-STA 409C thermal analyzer.

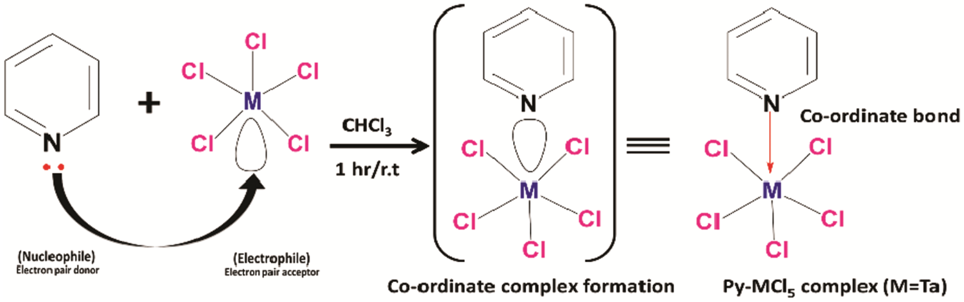
Synthesis of soluble pyridine-tantalum pentachloride complex (Py-$TaCl_5$)

The procedure for the preparation of pyridine-tantalum pentachloride complex as a Lewis acid (Py-$TaCl_5$) complex as given in Scheme 1: In a typical synthesis, 20 mmol (1.62 mL) of pyridine was mixed with 100 mL of chloroform in a 150 mL Round Bottom flask and then 20.0 mmol (7.16 g) of tantalum pentachloride was added carefully in a fuming cupboard without any loss. Then the contents of the flask were stirred for one hour at room temperature and the resulting colourless soluble Lewis acid complex viz., pyridine-tantalum pentachloride, (Py-$TaCl_5$) was filtered under vacuum and was washed with chloroform three times (3×100 ml). The obtained resultant viz., Py-$TaCl_5$ complex was colourless and hygroscopic in nature. Hence, it is stored in a vacuum desiccator (Yield = 60%). The formation of Py-$TaCl_5$ complex is established through UV-Vis, FT-IR and EDAX studies.

Synthesis of insoluble pyridine-based polymer-supported metal complex catalyst

The insoluble PSCPVP beads were prepared by adopting the procedure reported in the literatures[22-24]. It involved the suspension co-polymerization of styrene (supporting), divinylbenzene (crosslinking) and 4-vinyl pyridine (functional) monomers. For fixing 2% cross-linking (ratio of DVB) and 25 % active site (ratio of 4-VP), the organic phase was kept at 82.5 g and aqueous phase at 225 g. About 2.55 g of boric acid,1.35 g of gelatin and 2.25 g of PVA were dissolved separately in 60, 30 and 130 mL of de-mineralized hot water (50°C), respectively. Then, they were mixed together at 30°C. The blended solution was adjusted to *p*H 10 with the addition of 0.1 g sodium nitrite and 25% aqueous sodium hydroxide and then added to gelatin. It was transferred to a 250 mL three necked Round Bottom flask equipped with the overhead mechanical stirrer and the reflux condenser. Nitrogen gas was circulated continuously and the temperature was maintained at 50°C.

The organic phase containing 58.52 g of styrene, 3.3 g of DVB, 25.76 g of 4-vinylpyridine and 0.41 g of AIBN was mixed in a reaction flask After 30 min (maintaining the above condition). The thermostat temperature was raised to 70°C and the stirring was



Scheme 1 — Synthesis of soluble Pyridine – Metal chloride ($TaCl_5$) complex catalysts kept at 400 rpm. The reaction was continued for 48 hr. The resulting polymer beads were filtered through a Buckner funnel and washed with hot water and methanol repeatedly. Then, it was dried at 60^{o}C under vacuum condition for 48 hours and thus the cross-linked copolymer PSCPVP beads (Scheme 2) was obtained. Then, the polymer beads were sieved using RO-TAP testing Sieve Shaker and obtained particles at size viz., -60 + 80, -80 + 100, -120 + 170, -170 + 300 and above -300 mesh.

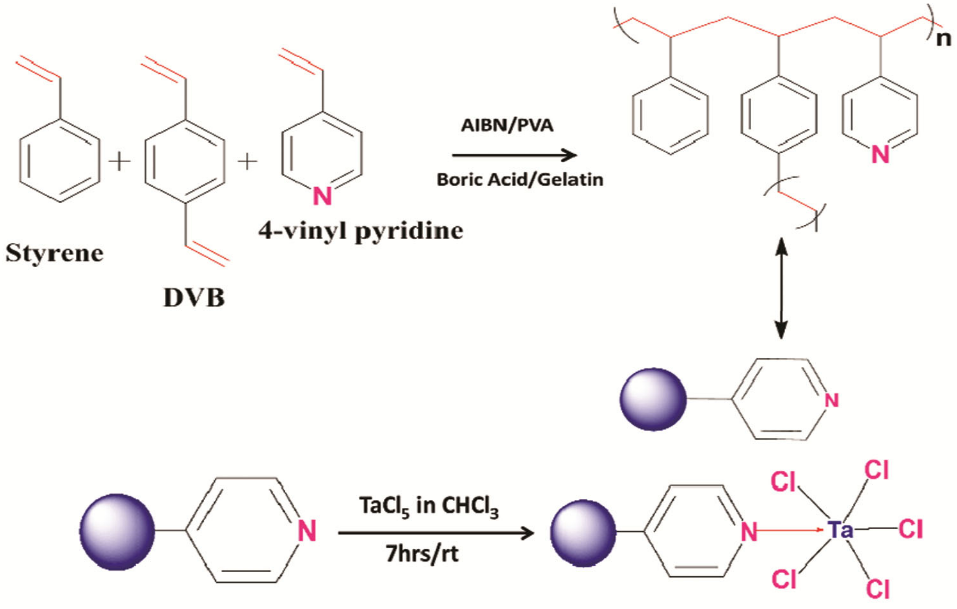
The procedure for the preparation of polymer-supported (4-vinlypyridine)-tantalum pentachloride complex (PSCPVP-$TaCl_5$) catalyst is as follows, the PSCPVP beads (3 g) were taken in a 150 mL Round Bottom flask and swelled in chloroform (100 mL) for 1 hr. To this mixture, 10 mmol (3.58 g) of tantalum pentachloride was added and stirred for hours at 30**°C** and then cooled between 0°-10°C. The resulting bead-shaped insoluble polymer-supported (4-vinyl pyridine)-tantalum pentachloride complex (PSCPVP-$TaCl_5$) catalyst was filtered and washed with acetone (Scheme 2). The catalyst was dried under vacuum at 50°C for 24 hr. The obtained PSCPVP-$TaCl_5$ beads were been characterized through FT-IR, elemental analysis, SEM and TGA analysis.

Catalytic efficiency of PSCPVP-$TaCl_5$ beads for Acylation reaction

The acylation was carried out in a 150 mL two necked RB flask in which ethanol (17.06 mmol) and acetic anhydride 33 mL (349.10 mmol) were taken. The flask was kept in a thermostat at 30 ± 1 °C and stirred at 400 rpm for ten minutes before the addition of the catalyst. A sample was collected from the reaction mixture at zero time. Then,0.45 mmol (0.3 g) of the insoluble catalysts was added to it. The samples have been taken and analyzed at regular intervals using GC. Kinetics of the reaction was followed by estimating the amount of ethanol disappeared using Gas chromatograph. The column used was five percent Chrom WHP 80/100, 3 m x 1/8” stainless steel tube. The flow rate of nitrogen was 30 mL /min. After sample injection, the column oven temperature was kept constant for 3 min at 60°C, then linearly raised to 160°C (30°C min^{-1}) and maintained at 30°C for the remaining time of analysis. The detector and injector temperatures were set at 270 and 250 °C, respectively. For each sample, the reaction mixture (0.5 μL) has been injected to GC and the products were analyzed; the RT (Retention Time) for ethanol was 1.47 min, acetic anhydride 4.21 min and the acylated product 1.37 min. The pseudo-first order rate constants were calculated by the plots of log (a-x) vs time, where (a-x) was the ethanol concentration at time t.

Kinetics of acylation of ethanol

The kinetics of acylation were studied with stable and insoluble PSCPVP-$TaCl_5$ catalyst with varying [substrate], stirring speed, [catalyst] and temperature under pseudo first order condition (Scheme 3). The stirring speed was varied in the range of 200 to



Scheme 2 — Preparation of PSCPVP-$TaCl_5$ beads

600 rpm and the [substrate], [catalyst] and temperature were kept constant. The rate constants were calculated. From the rate values, the optimum stirring speed was fixed as 400 rpm to conduct further kinetic study. Similarly, the substrate concentration was varied from 10.24 to 23.89 mmol keeping the remaining parameters constant. The amount of the catalyst was changed from 0.1 to 0.5 g, while the other kinetic parameters were kept constant. From the results, it has been demonstrated that 0.45 mmol (0.3 g) **as** the optimum catalyst concentration to study the other variable. The temperature was changed from 293 to 313 K and the other experimental parameters were kept constant and the temperature of 303 K was kept as optimum for the rest of the kinetic study.

Recovery and reusability of the catalyst

The stability and catalytic activity of the catalyst has been examined separately. The procedure for the study of reusability is as follows. In the acylation reaction, after the completion of reaction (i.e. first cycle), the catalyst has been recovered from the mixture by simple filtration, washed with methanol/acetone 3 times and then dried at 60°C. Then, the dried catalyst (recovered after first cycle) has been reused to conduct second cycle of acylation. As usual, the disappearance of ethanol is quantitatively followed through GLC irrespective of the catalyst and the pseudo-first order rate constants have been calculated. Again, after the second cycle, the catalyst is recovered and reused for the third cycle and the pseudo-first order rate constant is also calculated by maintaining the same experimental condition. On increasing the number of cycles, the pseudo-first order rate constant has been found to decrease gradually due to the leaching effect of $TaCl_5$ from polymer matrix. The leaching is not pronounced up to third cycle but after that, the catalytic efficiency has been decreased steadily. The calculated value of pseudo-first order rate constants of each cycle have been given in Table 3.

Scheme 3 — Acylation of ethanol with $TaCl_5$ on PSCPVP beads and acetic anhydride

Results and Discussion

Characterization of pyridine based homogenous (soluble) and heterogeneous (insoluble) tantalum chloride complex Lewis acid catalysts

FT-IR, UV-Visible and EDAX studies for soluble Py-$TaCl_5$ complex catalyst

In order to investigate the coordination reaction, individual FTIR spectrum of Pyridine and $TaCl_5$ has been recorded and compared with Py-$TaCl_5$complex. FT-IR spectrum of pyridine shows characteristic peaks at 1633 cm^{-1}, 676 cm^{-1} which corresponds to C=N(str) and C-H(str) of the pyridine unit. Similarly, the peaks at 1015, 1061, 1163 cm^{-1} and 1531, 1606 cm^{-1} have been attributed due to C-N(str) and C=C(str) respectively. After coordination reaction with $TaCl_5$ the FT-IR spectrum of Py-$TaCl_5$ (Fig. 1A) complex shows a lower shift in stretching frequency of C-N at 1628 cm^{-1} which corresponds to N-Ta metal stretching which confirms the interactions between the lone-pair of electrons in nitrogen atom of

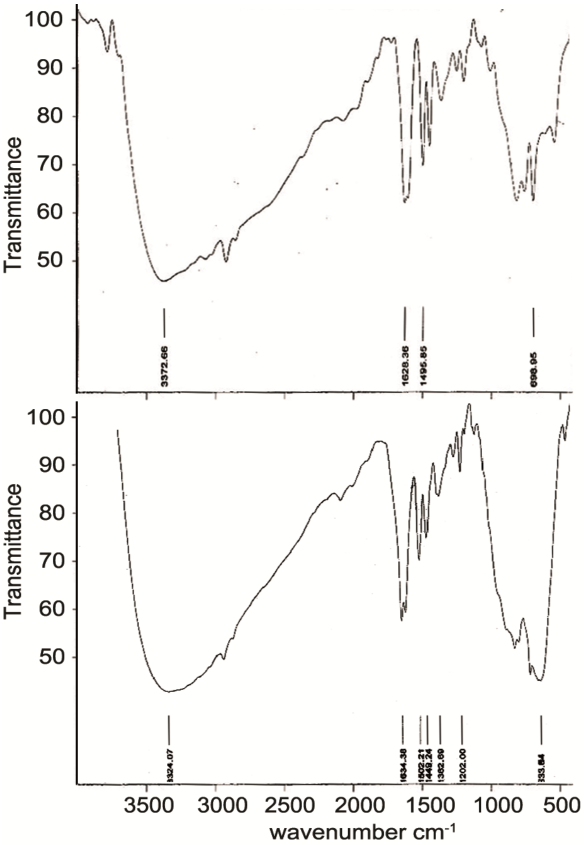


Fig. 1 — FT-IR spectrum of (a) Py-$TaCl_5$ and (b) PSCPVP-$TaCl_5$ Beads

pyridine with Tantalum. All these observations confirm the formation of the Ta metal complex catalysts (soluble catalyst) through co-ordination bond. The chemical binding can be ensured based on the corresponding absorption spectra of the metal complex. Therefore, in order to ascertain the chemical binding between $TaCl_5$ with pyridine, the pyridine-$TaCl_5$ complex catalyst have been dissolved in 0.25% methanol and then the solution is analysed with UV-Vis spectrophotometer in quartz cuvette. In the UV-Vis spectrum of pyridine-$TaCl_5$ complex, there has been a shift in the absorption band between 253-320 nm from 254 nm (pure $TaCl_5$) which corresponds to the binding of pyridine with Ta metal. Further, the elemental composition of soluble pyridine-$TaCl_5$ complex has been analysed using CHN analysis to determine the percentage of C, H & N and EDAX to identify the existence of Ta and chloride ions. The EDAX spectrum of Py-$TaCl_5$ shows characteristic peaks at 2.2 & 8.1 KeV for tantalum metal (Ta) and 2.8 KeV for chloride (Cl) which confirms the formation of Lewis acid complex with $TaCl_5$.

Structural interpretations of heterogeneous (Insoluble) tantalum chloride complex Lewis acid catalysts

FT-IR studies and CHN analysis

The FTIR spectrum of 4-vinylpyridine beads (PSCPVP) shows three characteristics peaks at 3019 cm^{-1} for aromatic C-H, 2921 cm^{-1} for aliphatic C-H and 1448 cm^{-1} for CH_2 bending respectively. Further, the PSCPVP beads shows peaks at 704 cm^{-1}, 1488 cm^{-1}, 1597 cm^{-1} due to the existence of C-N (str), C-N (str, ring), C=N (ring) groups respectively (Fig. 1B). These inferences confirm the incorporation of vinyl pyridine functionalization in the bead matrix. In addition, the formation of co-ordination bond between the nitrogen group of 4-vinlyl pyridine with $TaCl_5$ has been established through FT-IR studies. After the formation of Lewis acid catalyst (i.e.,) after the complexation between nitrogen group of 4-vinlyl pyridine in PSCPVP matrix with $TaCl_5$, the FTIR spectrum (Fig. 1b) shows a shift in stretching frequencies of C-N (str), C-N (str, ring), C=N (ring) groups to 633 cm^{-1}, 1449 cm^{-1}, 1634 cm^{-1} respectively which in turn confirms the co-ordination reaction. A similar type of observation was also reported by Balakrishnan *et al*. for the preparation of polymer supported catalysts with $SnCl_4$, $ZrCl_4$ and $TiCl_4$ respectively. Therefore, these observations clearly confirm the coordination of $TaCl_5$ to PSCPVP matrix. From CHN analysis it has been found that the plain PSCPVP beads have 87.93 % of Carbon, 8.09 % of Hydrogen and 4.10 % of Nitrogen respectively (Table 1).

Scanning electron microscopy (SEM) analysis

The immobilization of Lewis acid moiety viz., $TaCl_5$, onto the cross-linked 4-vinylpyridine functionalized poly(styrene) bead matrices have also been studied through changes in surface morphology of the beads. That is, the surface morphology of the plain beads viz., PSCPVP (Fig. 2a) has been compared with surface morphology of the PSCPVP-$TaCl_5$ (Fig. 2b). On comparison, it is observed that the surface morphology of the plain bead is found to be relatively smooth and homogeneous in nature, whereas, the complexed Lewis acid catalysts have shown drastic changes on the surface morphology. That is, the surface morphology of the complexed Lewis acid bead viz., PSCPVP-$TaCl_5$ shows a heterogeneous rough surface with white dots/patches which corresponds to the immobilization of Tantalum pentachloride through free electron of pyridine nitrogen functionalized in the cross-linked insoluble poly(styrene) matrices.

Table 1 — Elemental composition of insoluble PSCPVP and PSCPVP-$TaCl_5$ Beads

Acylation reaction	Stirring speed (rpm)	$k_{obs} \times 10^3$, min^{-1}
Variation of Stirring speed	200	4.35
	300	5.08
	400	9.88
	500	10.26
	600	10.37
Variation of [Substrate]	[Substrate] mmol	$k_{obs} \times 10^3$, min^{-1}
	10.24	4.64
	13.65	6.92
	17.06	9.88
	20.47	13.20
	23.89	16.71
Variation of [Catalyst]	[Catalyst] mmol	$k_{obs} \times 10^3$, min^{-1}
	0.15	7.25
	0.30	8.91
	0.45	9.88
	0.60	12.78
	0.75	14.64
Variation of Temperature	Temperature (K)	$k_{obs} \times 10^3$, min^{-1}
	293	5.69
	298	7.19
	303	9.88
	308	11.36
	313	14.32

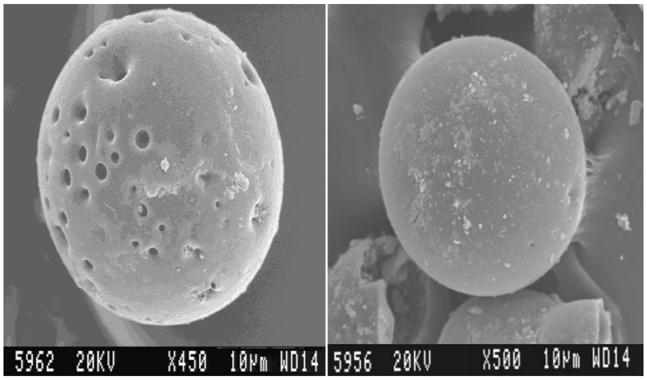


Fig. 2 — SEM images of (a) PSCPVP and (b) PSCPVP-$TaCl_5$

EDAX analysis

Further, the formation of co-ordination complex between the Tantalum pentachlorides with 4-vinyl pyridine substituted PSCPVP beads has also been confirmed through EDAX analysis. That is, the EDAX spectrum of PSCPVP beads (control) (Fig. 3A) has been compared with EDAX spectrum of PSCPVP-$TaCl_5$ complex catalyst (Fig. 3B) in which it has been noticed that in the control spectrum i.e. PSCPVP there has been no characteristic Cl and (or) any of the metal peak whereas, there is existence of Ta and Cl peaks in the case of PSCPVP-$TaCl_5$ complex catalyst. These observations strongly indicate the immobilization (or) formation of co-ordination complex between Tantalum pentachlorides and 4-vinylpyrdine substituted cross-linked poly(styrene) matrix.

Thermo gravimetric analysis (TGA)

In TGA analysis, $TaCl_5$ heterogeneous Lewis acid catalysts and PSCPVP beads (control) have been heated at controlled rate and then the percentage (%) of weight loss as well as thermal stability have been recorded as a function of temperature. From the TGA curves, the thermal stability of the raw beads (control) (Fig. 4A) as well as $TaCl_5$ Lewis acid complex catalysts (Fig. 4B) has been ascertained based on the obtained horizontal portion of the TGA. From the TGA results for PSCPVP beads (control), it has been observed that the beads undergo decomposition at three different stages. The first decomposition is observed between 180-310°C with 2.3% of weight loss, the second stage is found between 320-480°C with 88% of weight loss and finally third stage at 1000-1180°C with 3% weight loss. This observation reveals that the cross-linked 4-vinylpyridine substituted poly(styrene) beads i.e., PSCPVP has decomposed mainly at 320-480°C with weight loss of 88% In contrast, the thermogram of PSCPVP-$TaCl_5$ shows that the catalyst has decomposed at five different stages. In the first stage, i.e. between 100-180°C, the weight loss occurs at a rate of 13% and the second stage decomposition has been noticed between 180-300°C with 5.8% of weight loss; these two different decompositions must be due to the contribution of moisture and metal chlorides contents. The large weight loss of (42%) noticed between 290-520°C has been due to the decomposition of polymer matrix. Then, the two degradations between 520-1100°C and 1100-1350°C are due to the contribution of some charred carbon and oxide impurities. That is, the thermal stability of the catalyst

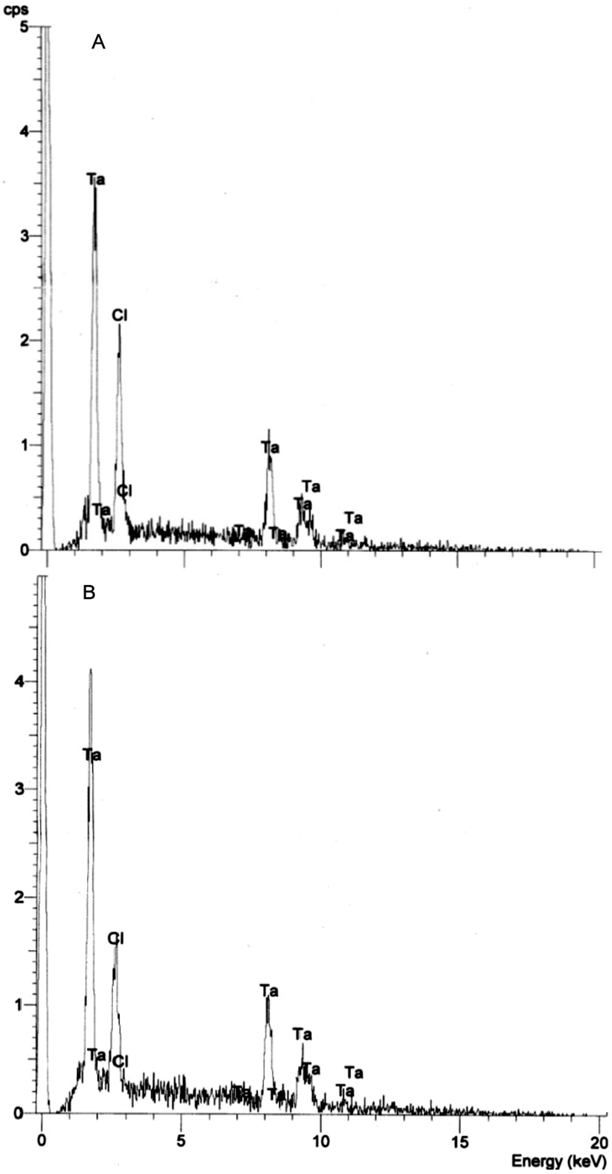


Fig. 3 — EDAX spectrum of (A) PSCPVP and (B) PSCPVP-$TaCl_5$

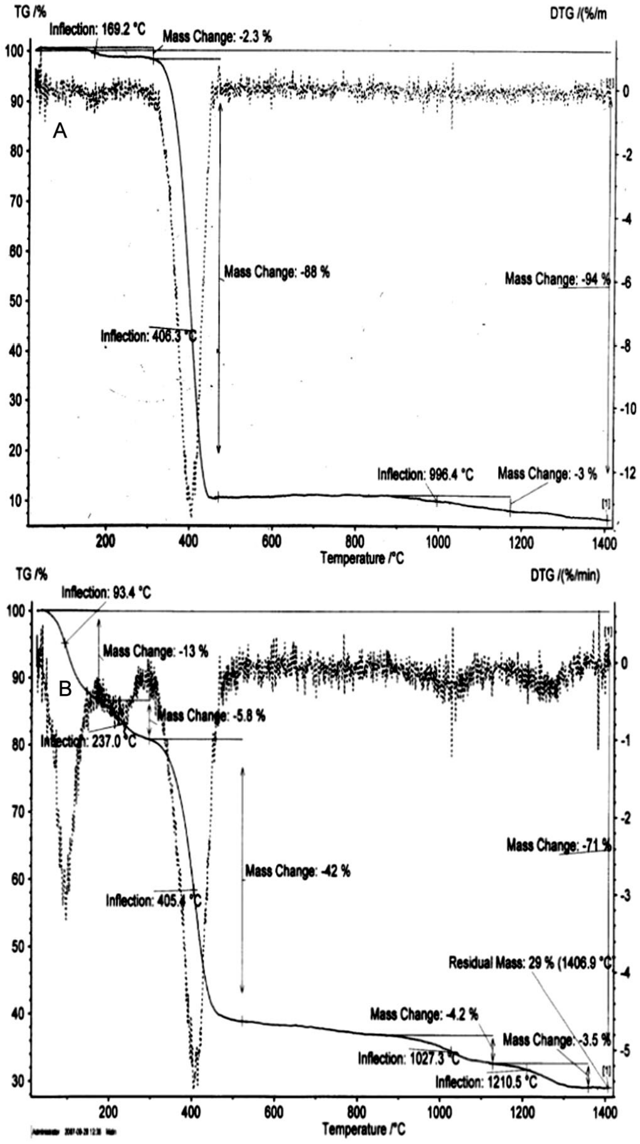


Fig. 4 — TGA and DTG curves of (A) PSCPVP Beads (B) PSCPVP-$TaCl_5$ Beads

in initial stage decomposition has been found to decrease with difference of 80°C as compared with control beads and thus indicating the immobilization of $TaCl_5$ on the polymer matrix.

Acylation of Ethanol with of Acetic Anhydride

The acylation of alcohols is a significant reaction in organic chemistry[25]. Acylation using acid anhydrides gives a cost-effective and efficient method for protecting hydroxyl groups during oxidation and coupling reactions[26]. Insoluble catalysts are very much useful for the sustainable development, catalyst recyclability and economic feasibility[27-30]. Q.Yao *et al.*[31] have reported a catalyst which is immobilized in 1-butyl-3-methylimidazolium with PF_6. Acylation of alcohols with Ac_2O catalysed by $TaCl_5$ has been reported by Chandraskear *et al.*[15].

In the present study, the kinetics of acylation of ethanol with acetic anhydride has been carried out in the presence of the insoluble PSCPVP-$TaCl_5$ complex. The reaction is experimented under pseudo-first order kinetics (taking acetic anhydride in excess) at 400 rpm between 293 and 313 K. The pseudo-first order rate constant has been evaluated from the log (a-x) vs time plot, where (a-x) is the concentration of ethanol at time 't'. Representative plots of log (a-x) versus time are given only for the variation of stirring speed for the entire system (Fig. 5A). The rate constant has been found to increase with increase in temperature. From the plot of log k_{obs} versus 1/T (Fig. 6D), the activation energy (E_a = 35.2 $kJ.mol^{-1}$) and the frequency factor (A = $1.07x10^7$ $lit.mol^{-1}$. s^{-1}) have been calculated. The other thermodynamic parameters, viz., the activation entropy ($\Delta S^{\#}$=-64.6 $JK^{-1}.mol^{-1}$), activation enthalpy ($\Delta H^{\#}$=37.7 KJ. mol^{-1}) and free energy of activation ($\Delta G^{\#}$ =57.3 kJ mol^{-1}) are also calculated.

Effect of stirring speed

The effect of variation in the stirring speed on the rate of acylation of ethanol with acetic anhydride using PSCPVP-$TaCl_5$ has been studied in the range 200 to 600 rpm and the results are shown in Table 2. The reaction rate increases with the increase in the stirring speed and pseudo-first order rate constant is calculated from the log (a-x) vs time plots (Fig. 5A). A plot of rate against stirring speed is illustrated in Fig. 6A. Initially, the rate constant for acylation increases slowly from 200 to 300 rpm, then increases rapidly and reaches a maximum rate at 400 rpm. There is no change in the rate above 400 rpm. That is, even though the active sites are found on the surface when the mixture is stirred mechanically; a mild increase of rate from 200 to 300 rpm is attributed to an increase in the contact between the substrates and catalyst. At 400 rpm, a sudden increase in rate has been observed due to high mass transfer from bulk liquid to catalyst active sites and again at 600 rpm onwards that is only very minor increase in rate due to steady level of mass transfer. This denotes that 400 rpm is the optimum one. So, 400 rpm is kept as the optimum one for other kinetic variations. Similar type of observations has been noted for the kinetic study of acylation of resorcinol along with acetic acid using ion-exchange resin as a catalyst with the stirring speed from 800 to 1200 rpm.[32]

Effect of [substrate]

Kinetic experiments have been carried out by varying the concentration of ethanol from 10.24 to 23.89 mmol maintaining other reactant such as acetic anhydride excess. The pseudo-first order rate constant is evaluated from the log (a-x) vs time plot (Fig. 5B). The rate increases with the increase in the concentration of ethanol (Fig. 6B). It is due to the increase in the absorption of substrate molecules on the surface of the catalyst. Neckers *et al.*[33] have also reported similar observation in the esterification butanol using various acids such as acetic acid, propionic acid and benzoic acid using polystyrene supported aluminium chloride as a catalyst. It is also reported that the rate of acylation of p-cresol and anisole depends on the substrate concentration in the esterification[34, 35].

Effect of catalyst loading

The effect of loading of PSCPVPV-TaCl$_5$ complex catalyst has been studied in the range 0.1 g to 0.5 g. The rate constants are evaluated from the log (a-x) vs time plots (Fig. 5C) and the results are shown in Table 2. The observed rates have been plotted vs the amount of the catalyst is added. A linear dependence is observed (Fig. 6C). This is due to enhancement in the total number of available Lewis acid sites on the catalyst surface with the increase in catalyst loading. Similar observations have also been reported for the acylation of *p*-cresol using H$_2$SO$_4$and4-nitrophenol with acetic acid using Pd catalyst on increasing the catalyst load.[36]

Effect of temperature

The rate constant of acylation has been measured at different temperatures viz., 293, 298, 303, 308 and 313 K by employing 0.43 mmol of insoluble PSCPVP-TaCl$_5$ catalyst. The rate constants are derived by plotting log (a-x) vs time for each temperature (Fig. 5D) and the results are given in Table 2. The rate constant increases with the increase in temperature. From the plot of log k$_{obs}$ versus 1/T (Fig. 6D), the activation energy (E_a = 35.2 kJ.mol^{-1}) and the frequency factor (A = 1.07x10^7 lit.mol^{-1}. s^{-1}) have been calculated. Other thermodynamic parameters, viz., the activation entropy ($\Delta S^{\#}$=-64.6 JK^{-1}.mol^{-1}), activation enthalpy ($\Delta H^{\#}$=37.7 KJ. mol^{-1}) and free energy of activation ($\Delta G^{\#}$ =57.3 kJ mol^{-1}) have also been calculated.

G.D. Yadav *et al.*[32] found a substantial increase in the rate of acylation on increasing the temperature due to increase in formation of carbocation. Similar enhancement in rate is also observed by S. Mayadevi *et al.*[35] in the pseudo-first order reaction of acylation

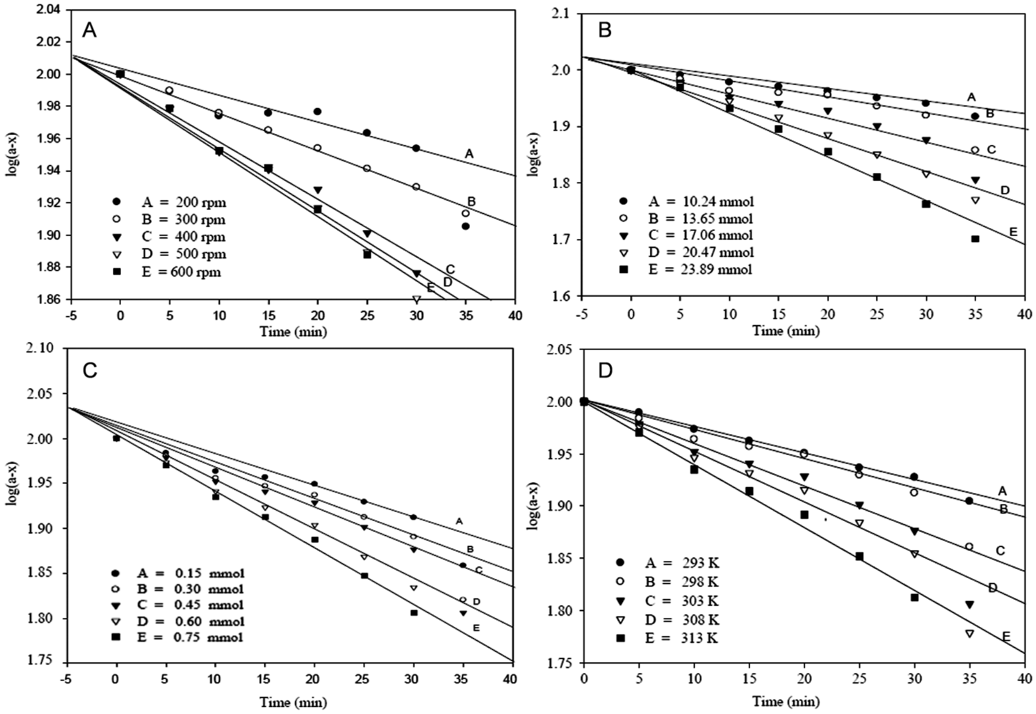


Fig. 5 — Plots of log(a-x) Vs time for effect of (A) stirring speed, (B) [substrate] variation, (C) catalyst variation and (D) temperature for Acylation of ethanol with acetic anhydride

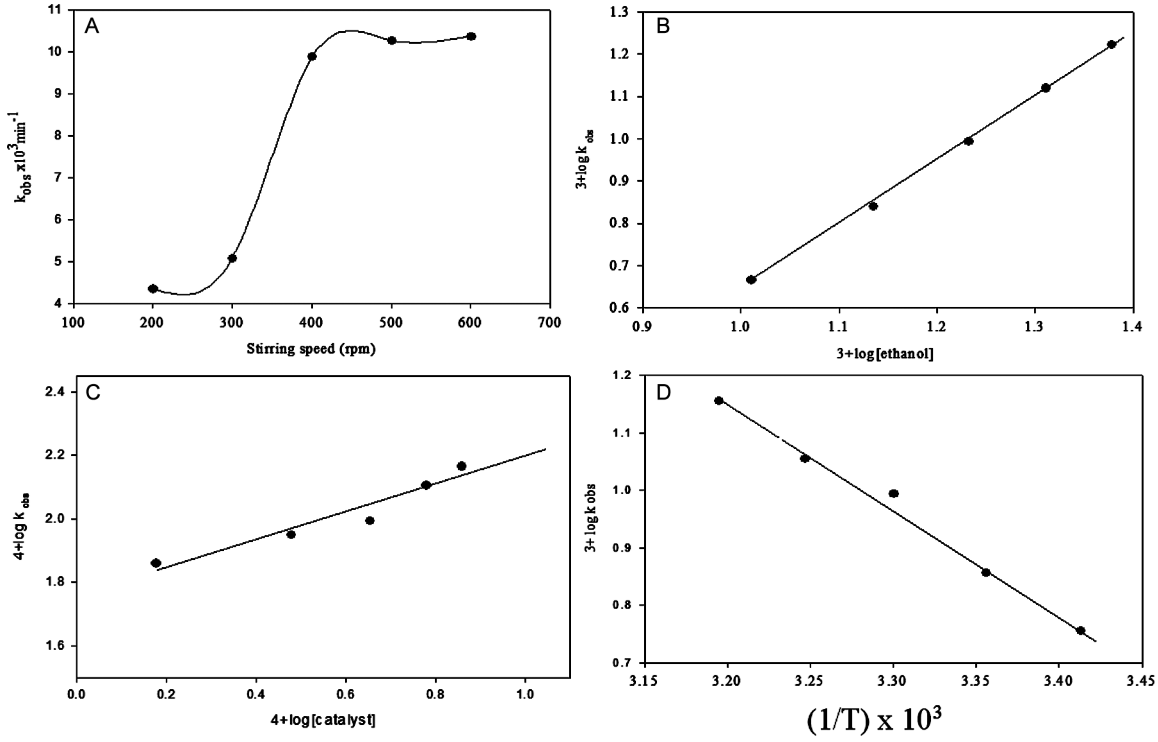


Fig. 6 — Plots for effect of (A) Stirring speed, (B) [Substrate] variation, (C) Catalyst variation and (D) Arrhenius Plot - temperature variation on k_{obs} values for Acylation of ethanol with acetic anhydride

Table 2 — The pseudo-first order rate constant for acylation of ethanol with acetic anhydride using PSCPVP – $TaCl_5$ catalyst

Name of the bead	N (%)		C (%)		H (%)		$TaCl_5$ (%)	
	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp
PSCPVP (control)	4.10	3.58	87.93	87.75	7.97	8.09	0.00	0.00
PSCPVP-$TaCl_5$	2.00	1.56	42.91	40.00	3.89	4.79	51.19	53.65

Table 3 — Comparative catalytic efficiency of soluble and insoluble catalysts for acylation of ethanol with acetic anhydride

No. of cycles	Py - $TaCl_5$ k_{obs}x10^3,min^{-1}	PSCPVP- $TaCl_5$ k_{obs}x10^3,min^{-1}
1	11.42	6.98
2	-	6.85
3	-	6.79

of anisole with carboxylic acids over zeolites and have reported E_a of 63.2 kJ mol^{-1} for the formation of ester. Yamanaka and Imai[37] have also studied the temperature dependence of rate constant for acetylation. The influence of temperature on the acylation of phenol with the acetic acid has been studied by Sobrinho *et al.*[38] and they have proved that the high temperatures favoured the formation of product viz., phenyl acetate.

Mechanism of Acylation

The reaction rate of the insoluble polymer supported catalyst is limited by the factors like i) diffusion of reactants towards the active catalytic surface, ii) adsorption and activation of reactants on the catalyst surface, iii) conversion of reactants into products, iv) diffusion of products away from the catalyst surface. The reaction shows high negative entropy and such a high negative value indicates that the catalyst, acetic anhydride and ethanol probably produce a more ordered transition state.

Conclusion

It is inferred that the Lewis acid complex catalysts employed for acylation are found to proceed effectively irrespective of soluble and insoluble nature of Lewis acid complex catalysts. The obtained k_{obs} reveals that reaction rates have been found to increases with the increase in the stirring speed, [substrate], [catalyst] and temperature. The thermodynamic parameters viz., activation energy (E_a), entropy ($\Delta S^{\#}$), enthalpy ($\Delta H^{\#}$) and free energy ($\Delta G^{\#}$) for the reaction have also been calculated for the first time. In the acylation, after the completion of the reaction (i.e. first cycle), the polymeric insoluble PSCPVP-$TaCl_5$ catalyst has been easily separated from the reaction mixture by easy filtration and reusable for 3 times with good catalytic activity. The polymeric catalyst is stable and can be easily recovered and reused without appreciable change in its effects. The same catalyst can also be exploited to catalyse the acylation of other primary alcohols. Its applicability to acylation of secondary and tertiary alcohols is to be examined in future. In addition, modified catalysts can also be prepared and tested by employing other pyridine based derivatives. The reaction can be tested for N-acylation of aliphatic and aromatic amines and O-Acylation of phenols and its derivatives. Excellent yields, cheap and readily available reagents and easy workup are the advantages of the present study. Finally, this polymer supported transition metal catalyst PSCPVP-$TaCl_5$ and their applications are of greater importance for industrial processes.

Conflict of Interest

There are no conflicts to declare.

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