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Efficient soluble and polymer cross linked insoluble poly-4-vinyl pyridine metal(V) chloride catalysts for esterification of butanol with acetic acid

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New soluble and insoluble Ta, Mo and Sb pentachloride complex catalysts have been prepared using pyridine and polymer supported cross-linked (poly-4-vinyl pyridine) beads (PSCPVP), respectively. The prepared catalysts are characterized with FTIR, SEM, EDAX, CHN and TGA. The catalytic activities of these catalysts have been examined for esterification of acetic acid with butanol through gas chromatographic technique. The soluble complex catalyst show better activity than the insoluble catalyst, but it suffers from recovery and recyclability. The insoluble catalysts maintain stability up to three recycle times. From the k_{obs} values, it is found that all the soluble catalysts of Py-MCl_5, M=Ta, Mo & Sb (k_{obs}=7.26, 5.48 & 1.47×10^3 min^{-1}) showed higher catalytic activity than the insoluble PSCPVP-MCl_5 (k_{obs}=5.18, 2.24 & 0.87 $x10^3$ min^{-1}), but the latter catalysts are superior to the former in terms of recyclability. The catalytic activity of soluble Py-$TaCl_5$, Py-$MoCl_5$, Py-$SbCl_5$ catalyst is found to be 1.40, 2.44 and 1.68 times higher than PSCPVP-$TaCl_5$, PSCPVP-$MoCl_5$ and PSCPVP-$SbCl_5$, respectively. PSCPVP-$TaCl_5$ catalyst is found to be the superior most catalyst among the three catalysts. Further, these catalysts can be used in column batch reactors to conduct the reaction in continuous mode.

Keywords: Esterification, Polymer supported metal complex catalyst

Synthesis of esters through esterification of carboxylic acids and acylation of alcohols has been an attractive/effective organic transformation reaction. Particularly, the demand for esters has been increasing day-by-day owing to their vital applications in various arenas including pharmaceuticals, intermediates, artificial perfumes and lacquers. In view of the significance of the ester products and their current requirements in larger quantities, the study on esterification reaction with suitable means was considered to be an adoring area of interest. Normally, these reactions are performed with the help of different catalysts which include mineral acids, inorganic complexes and the organometallic Lewis acid complex catalysts. Several catalysts and methods have been already available to accelerate these reactions but the reaction that proceeds with the aid of homogeneous Lewis acid complex catalysts is more effective than any others. Specifically, heterogeneous metal complex Lewis acid catalyst could definitely be an environmentally benign, cost effective and convenient one to perform the esterification with larger quantities. Therefore, the synthesis of Lewis acid complex catalysts using metal halides with suitable ligands was found to be an attractive method to facilitate esterification.

However, while designing the effective Lewis acid complex catalysts (both homogeneous and heterogeneous), the characteristics of the metal halide and ligands should be the prime concern to generate Lewis acidity in the complex catalysts. Transition metals have several features unlike representative metals, most of them have variable oxidation states as well as coordination number and thus show an excellent character to form Lewis acid complex[1,2]. The transition or non-transition metal in the form of chloride can easily form the Lewis acid complex catalyst with basic ligands[3]. Similarly, the molecules containing heteroatom like pyridine, butylamine and indole are an important unit of basic character and hence used as effective ligands and thus form an efficient Lewis acid complex catalyst with different transition metal halides.

In fact, in recent years, the application of soluble (homogeneous) Lewis acid complex catalysts and insoluble polymer-supported transition Lewis acid metal complex catalysts (heterogeneous) in commercial industrial processes has become a common practice. Particularly, the heterogeneous catalysts derived from insoluble polymer matrix has overcome the problem of catalyst recovery and again if the expensive metals are immobilized, then without the loss of the catalyst, they can be conveniently recycled and also be reused sequentially in one-step to carry out multistep catalytic organic synthesis and in turn avoid the intermediate purification steps. In particular, because of these merits, they have been used as catalysts for a wide range of reactions, principally for olefinic substrates, including esterification, acylation, acetalizaiton, ketalization, hydrosilylation, carbonylation, acetoxylation, hydroformylation, polymerization and hydrogenation[4]. More particularly, the industries are expected to have an effective and convenient shape of insoluble heterogeneous Lewis acid complex catalysts to perform the esterification reaction in continuous mode operation using column/batch reactors.

In fact, the extensive literature survey on polymer-based heterogeneous Lewis acid complex catalysts reveals that there is no report for the preparation of bead-shaped microporous cross linked poly(styrene) network functionalized with 4-vinylpyridine as a matrix (ligand) and immobilized with transition/non-transition metal (central metal) based chlorides like $TaCl_5$, $MoCl_5$ and $SbCl_5$ for effective catalysis of esterification reactions. With these background, the present work describes the synthesis and characterization of three different soluble and three different insoluble catalysts. Further, the catalytic activity of all these six catalysts was assessed for esterification of butanol with acetic acid under pseudo-first order reaction condition.

Materials and Methods

Chemicals

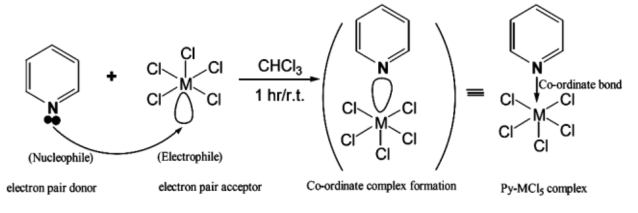
Styrene (Fluka) and divinylbenzene (Fluka)) were used as such in the preparation of polymer beads. The monomer, 4-vinylpyridine (Fluka), was distilled under reduced pressure and used for the preparation. AIBN (Koch-light, USA) was recrystallised from ethanol. Gelatin (BDH), boric acid (Merck), polyvinyl alcohol (Fluka), NaOH (SRL), $NaNO_2$ (SRL),$TaCl_5$(Lancaster), $MoCl_5$ (Strem) and $SbCl_5$ (Strem) acetic acid (Merck), chloroform, methanol, acetone, butanol and other organic reagents were purified according to the standard procedure.

Characterization techniques

All the FTIR spectra were recorded on Bruker Tensor-27 FTIR spectrophotometer with OPUS software. The sampling was done using KBr pellets with required amount of sample, the background calibrations have been carried out using pure KBr pellet. CHN analysis was conducted on Elementar Vario EL III CHN Analyzer. SEM images were recorded on HITACHI S-3000H Scanning electron microscope operated at different electron volts with different distances. A strip of double sided conducting carbon tape was applied to the metal stub and the samples were deposited on the carbon tape after that sample was allowed to scanning. SEM analysis was carried out for polymer-supported metal complex catalysts, PSCPVP-MCl_5, having mesh size of +80-100 and compared with plain PSCPVP beads of same mesh size. Since polymeric metal complex catalysts are electrically non-conducting, they should be made conductive by gold coating. The respective complex catalysts were spread on the surface of double sided adhesive tape, one side of which was already adhered to surface of a circular copper disc pivoted by a rod. HITACHI S-3000H auto fine-coating ion sputter was used for the gold coating under identical experimental conditions. The thermogravimetric analyses were carried out in a ZETSCH-STA 409C thermal analyzer.

Synthesis of soluble Py-MCl_5 Lewis acid catalyst

In a 150 mL single-necked RB flask, 20 mmol of pyridine was dissolved in 100 mL of chloroform. To this homogenous solution, 20 mmol of metal pentachloride was carefully added using fuming cupboard. The reaction mixture in the flask was stirred using a magnetic stirrer for 1 h at room temperature. The resulting soluble pyridine-metal pentachloride (Py-MCl_5) Lewis acid complex catalyst was filtered under vacuum and washed repeatedly with chloroform (3×100 mL). The obtained Py-MCl_5 complex catalyst (Scheme 1) was hygroscopic in nature, and hence it was stored in a vacuum dessiccator. The yield of Py-$TaCl_5$, Py-$MoCl_5$ and Py-$SbCl_5$ was 60, 48 and 35%, respectively.



Scheme 1 — Synthesis of soluble Py-MCl_5 Lewis acid catalysts [M= Ta,Mo and Sb]

Synthesis of polymer PSCPVP beads

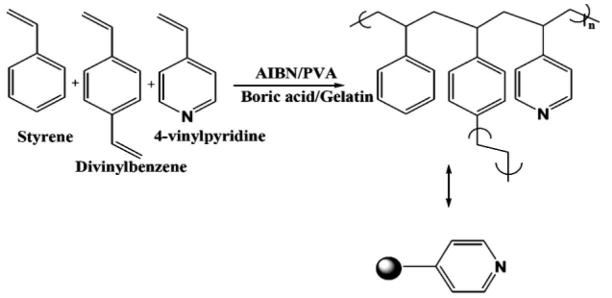
This insoluble polymer-supported cross linked poly (4-vinylpyridine) (PSCPVP) beads were prepared by adopting the early procedure in literature[5]. The method involves the suspension copolymerization of styrene (supporting), divinylbenzene (crosslinking) and 4-vinyl pyridine (functional) monomers. By fixing 2% crosslinking (ratio of DVB) and 25% active site (ratio of 4-VP), the organic phase was maintained at 82.5 g and aqueous phase at 225 g. Exactly 1.35 g of gelatin, 2.55 g of boric acid and 2.25 g of polyvinyl alcohol were thoroughly dissolved individually in 30, 60 and 130 ml of double distilled hot water (50°C). The dissolved polyvinyl alcohol maintains the viscosity of the medium. Then these solutions were mixed together at room temperature. The pH of the mixed solution was adjusted to 10 with the addition of 25% aqueous sodium hydroxide solution and then 0.1 g sodium nitrite was added to maintain the conformation of gelatin. The aqueous phase became clear only after adjusting the pH to 10. It was then transferred to 250 mL three necked RB flask equipped with an overhead mechanical stirrer and a reflux condenser. Nitrogen was passed continuously and the temperature was maintained at 50°C. After half an hour (maintaining the above condition), the organic phase containing 3.3 g of DVB, 58.52 g of styrene, 25.76 g of 4-vinylpyridine and 0.4125 g of AIBN was thoroughly mixed and added to the reaction flask. The blade level of the stirrer was adjusted so that the tips were in organic phase and most of the blade in aqueous phase. Subsequently, the thermostat temperature was increased to 70°C and the stirring speed was maintained at 400 rpm using tachometer. The polymerization reaction was allowed till the completion of 48 h (Scheme 2). The resulting polymer beads were filtered through a Buckner funnel and washed with hot water and cold methanol repeatedly until the wash solution did not turn cloudy upon the addition of water. Then it was dried at 60°C in a vacuum oven for 2 days and thus obtained insoluble crosslinked copolymer PSCPVP beads. Then, the polymer beads were sieved using RO-TAP testing Sieve Shaker (W.S. Tyler Company, and Cleveland, Ohio) and thus obtained different particle size viz., -60 + 80, –80 + 100, –120 + 170, -170 + 300 and above –300 mesh.

Immobilization of MCl_5 on to PSCPVP beads

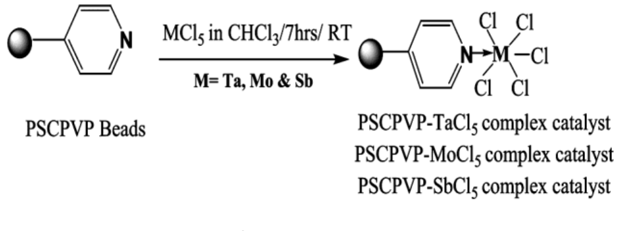
The insoluble PSCPVP beads (3 g) were swelled in chloroform (100 mL) for 1 h in a 150 mL RB flask fitted with a guard tube containing anhydrous calcium chloride and to which 10 mmol of metal pentachloride was added[16]. The resulting reaction mixture was stirred for 7 h at room temperature and then cooled to 0-10°C and thus yielding the pale yellow coloured polymer-supported (4-vinlypyridine)-niobium pentachloride complex Lewis acid catalyst (PSCPVP-MCl_5) which was filtered and then washed with chloroform and acetone so as to remove the unreacted MCl_5. The PSCPVP-MCl_5 catalyst was further dried under vacuum at 50°C for 24 h. The preparation of PSCPVP-MCl_5 complex catalyst is given in Scheme 3.

Esterification of butanol with acetic acid

The esterification reactions were carried out in a 150 mL two necked round bottom flask which was charged with excess of acetic acid i.e., 30 mL (524.6 mmol) and 1 mL (10.93 mmol) of butanol. The flask was placed in thermostat maintained at required temperature and stirred at 400 rpm for 10 min to condition the substrates, before adding the catalyst. A sample was drawn from the reaction mixture (zero time). Then, 0.25 mmol of each soluble catalyst such as Py-MCl_5, and PSCPVP-MCl_5 was added individually to the reaction mixture and then the reaction was allowed to proceed by means of constant stirring and temperature. The samples of each catalyzed reaction were collected at regular intervals of time and then the respective reaction mixtures were analyzed using GC. The kinetics of the reaction was followed by estimating the amount of butanol disappeared using gas chromatograph. The column used for the analysis was 2.5% PEG-2000 + 25% silicone DC-550 Celite-



Scheme 2 — Insoluble crosslinked PSCPVP Beads (Matrix)



Scheme 3 — Synthesis of insoluble polymer-supported PSCPVP-MCl_5 catalysts

545 CH.WHP 45/60, 2 m × 1/8″ with pre-column length of 4″. Nitrogen was used as a carrier gas at a flow rate of 30 mL/min. After the injection of sample for analysis, the temperature of the column oven was kept constant for 5 min (90°C), then linearly increased to 120°C (10°C min^{-1}) and kept at this temperature for the remaining time of analysis. Injector and detector temperatures were set at 250 and 270°C, respectively. For every sample, 0.5 µl of reaction mixture was injected to the column and the products were analyzed; the retention time for butanol was observed at 3.3 min, acetic acid at 4.06 min and the ester (product) was noticed at 7.47 min.

Results and Discussion

Characterization of the catalysts by FTIR

The formation of complex or coordination bond between pyridine and the respective metal chlorides in all the three different complex catalysts has been established through their respective FTIR spectra. The spectrum of each complex catalyst was compared with the FTIR spectrum of plain pyridine (Fig. 1) and the respective pure metal chlorides (control). That is, the FTIR spectrum of pyridine corresponds to C=N stretching of the pyridine unit. Similarly, the FTIR spectrum of metal chlorides viz., $TaCl_5$, $MoCl_5$ and $SbCl_5$ showed peaks at 1633, 1622 and 1621 cm^{-1}, respectively. The FTIR spectrum of the three metal complex catalysts yielded a new peak at 1628 cm^{-1} for Py-$TaCl_5$, 1633 cm^{-1} for Py- $MoCl_5$ and 1633 cm^{-1} for Py-$SbCl_5$ (Fig. 1 A-C) which corresponds to N-Metal stretching and thus confirming the interactions between the lone-pair of nitrogen of pyridine with respective metals. Thus, the appearance of new peaks in the spectrum of each Lewis acid complex catalyst undoubtedly confirms the formation of the respective metal complex catalysts shows the peak at 1587 cm^{-1} which through coordination bond. Aranaldo Costa Faro Jr *et al.*[5] had prepared the alumina-supported niobia metal catalysts in which they observed that the metal complex gives different characteristic peaks at 1450, 1490, 1575 and 1620 cm^{-1} and thus confirming the formation of coordination bond between pyridine and aluminium, whereas, the free pyridinium ions show a peak at 1580 cm^{-1}. The same trend of FTIR results was also reported by Belfiore *et al.*[6] for the transition-metal coordination complexes of poly (4-vinyl-pyridine) and dichlorotricarbonyl ruthenium(II). That is, the C=N stretching frequency of free pyridine was identified at 1598 cm^{-1}, while the complex gives a peak at 1615 cm^{-1}. Spinelli *et al.*[7] prepared synthetic macromolecule-metal complexes catalyst by simply mixing the copper metal cations with poly-(4-vinylpyridine). They also found the characteristic stretching frequency of pyridine rings at 1600 cm^{-1} for pure poly (4-vinylpyridine) and for complex, the vibration mode has been shifted to 1618 cm^{-1}, and thus suggesting the coordination between the pyridinic nitrogen and the copper metal. Pandurangan *et al.*[8] also observed a high-intensity peak around 1620 cm^{-1} for pyridine adsorbed on Lewis acid sites for mesoporous heterogeneous Al-MCM-41 catalysts.

EDAX analysis

It is known that energy dispersive X-ray analysis is one of the most effective characterization techniques for identifying and quantifying the surface elements in a semi-quantitative fashion. Hence, all the Lewis acid

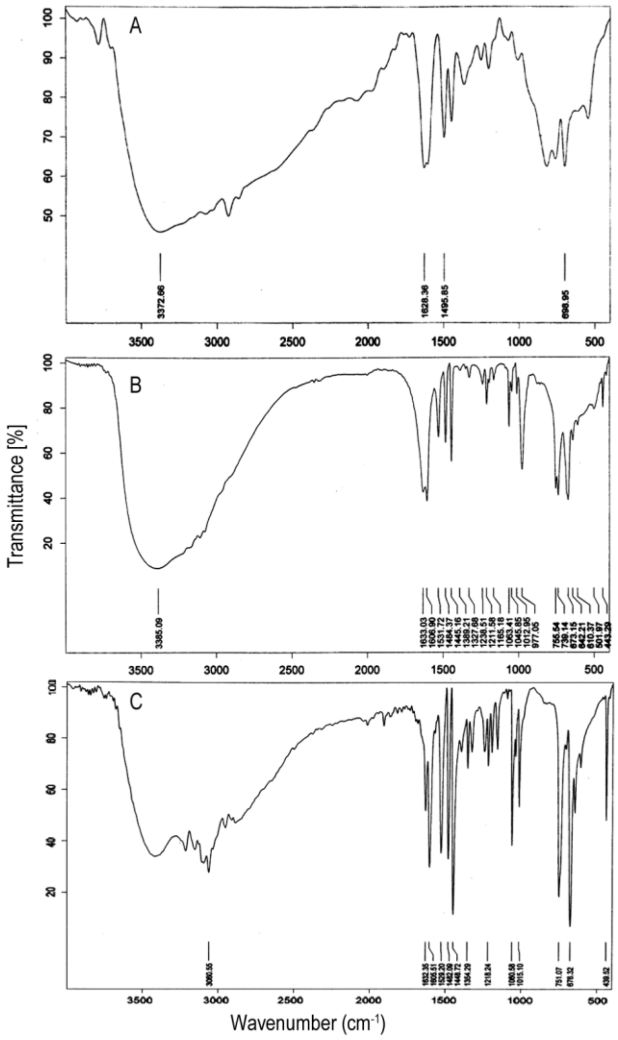


Fig. 1 — FTIR spectra of (A) Py-$TaCl_5$, (B) Py-$MoCl_5$ and (C) Py-$SbCl_5$

complex catalysts were characterized with EDAX analysis. The EDAX spectrum of three Lewis acid complex catalysts viz., Py-TaCl$_5$ (Fig. 2A) showed three characteristic peaks at 2.2 & 8.1 KeV for tantalum metal (Ta) and 2.8 KeV for chloride (Cl), Py-MoCl$_5$ (Fig. 2B) yielded two characteristic peaks at 2.4 and 2.8 KeV and these in turn corresponds to molybdenum metal (Mo) and chloride (Cl) respectively. In the case of Py-SbCl$_5$ (Fig. 2C), there are three major characteristic peaks at 3.5 & 4.1 and 2.8 KeV which corresponds to antimony metal (Sb) and chloride (Cl), respectively.

Zheng[9] synthesized poly(N-2-thiazolyl-acrylamide) supported Fe(II) and Nd(III) complex catalysts and observed similar type of results in their EDAX spectra. Similarly, the EDAX spectrum of polymer-metal complexes obtained by radiation-induced grafting process onto polyester fabrics using transition metals also confirmed the formation of complex. Zohdy[10] also established the availability of silicon metal peak in the EDAX spectrum of poly(methyl methacrylate) and poly(styrene) coated on the surface of synthetic fibre. Ruckenstein & Hong[11] support the EDAX result for the assessment of surface chloride of polymer-supported phase transfer catalyst based on the peak intensity (chloride). Balakrishnan & Murugan[12] suggested a similar type of EDAX results for surface-enriched (with active sites) polymer-supported phase transfer catalysts in which the increase in the intensity of chloride peak indicates the surface enrichment of active sites. Normally, the ability of the formation of coordination complex depends on the structure and chemical behaviour of ligands and central metal atom. Particularly, the formation of transition metal coordination complex with different basic ligands has been recognized as an effective Lewis acid complex catalyst. In our study, Lewis acid reagents viz., TaCl$_5$, MoCl$_5$ and SbCl$_5$ were not used directly as they are unstable, corrosive and moisture sensitive. The ligand (pyridine unit) containing unshared electron pair (n) in N atom and the transition metal atom containing higher coordination number are supposed to be the effective factor for the formation of thermo-dynamically stable Lewis acid metal complex catalyst. It is also understood from the literature that the transition metals are excellent Lewis acids and accept the electron density from many molecules or ions that act as Lewis base[13,14]. Therefore, in our case, the metal present in selected Lewis acid metal chlorides i.e., Ta, Mo and Sb also have more than six coordination number along with different oxidation states. Ooi *et al.*[15] prepared the [Nb(edta)(H$_2$O)$_2$].2H$_2$O complex and suggested that the formation of effective complex is due to eight coordination of Niobium metal. Similarly, Michael *et al.*[16] also prepared the [Nb(S$_2$ CNEt$_2$)$_4$]Br and [Ta(S$_2$ CNEt$_2$)$_3$] (S$_2$) complexes and they established has exhibited more than eight coordination number for Nb and Ta. Likewise, the pyridine ligand also contains unshared electron pair (n) and thus it is expected to form an effective Lewis acid complex catalyst irrespective of metal penta chlorides[7-17]. More particularly, the pyridine has been extensively studied because of the capacity to show hydrophilic properties, chemical reactivity and the ability to form complex[18].

All the observed spectral results viz., UV, FTIR, and EDAX confirmed the formation of Lewis acid complex irrespective of the metal chlorides. That is, the characteristic absorption band such as Py-M noticed in the UV, the appearance of N-M stretching in FTIR and the peaks for metal and halides (Cl) with

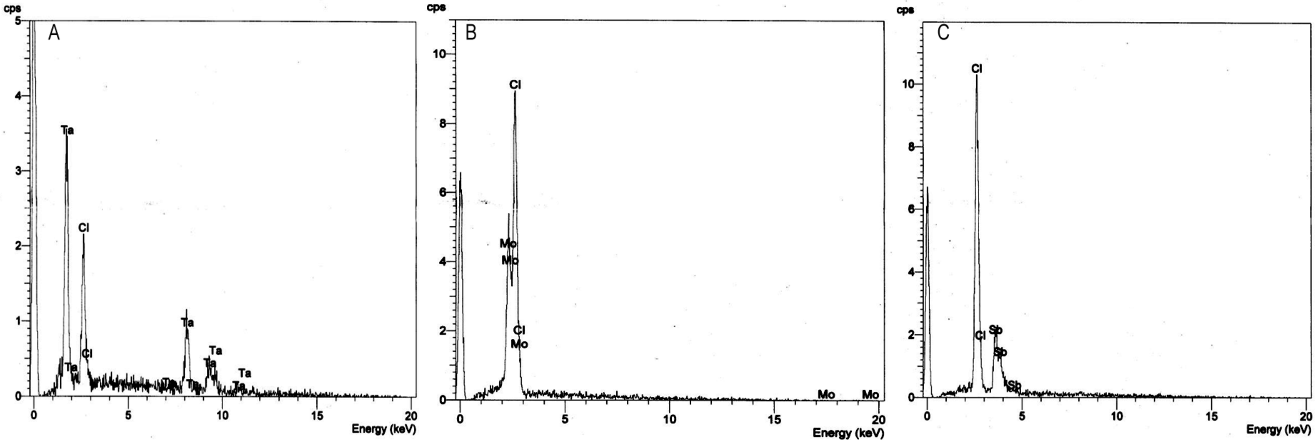


Fig. 2 — EDAX analysis of (A) Py-TaCl$_5$; (B) Py-MoCl$_5$; and (C) Py-SbCl$_5$

different electron volt noticed in EDAX analysis strongly confirmed the formation of coordination bond between the unshared electrons in N-atom of pyridine with the respective metal chlorides. Further, from the earlier literatures, it was understood that the possible chemical bond during the formation of Lewis acid complex has reported to be (i) $\pi \rightarrow$ Metal complexes, ii) n → Metal complexes and iii) polymer-bonded complex. In our case, the unshared electron present in the nitrogen atom of pyridine is more active than the π bond present inside the pyridine ring. Hence, the formation of complex between pyridine and metal chlorides must be coordinated by n → metal complex type irrespective of the metal chlorides. That is, all the selected metal pentachloride has five coordination number, further, on addition of pyridine ligand irrespective of metal halide the 6th coordination has formed via n → metal complex. But still, since all the metal pentachlorides have more than six coordination number, we strongly expected the Lewis acidity in each Py-M Lewis acid complex catalyst. The Lewis acidity/catalytic activities of these complex catalyst have been examined by estimating the pseudo-first order rate constant of esterification of acetic acid with butanol.

Synthesis and characterization of heterogenous (insoluble) Lewis acid metal complex catalysts using 4-vinylpyridine functionalized bead-shaped poly (styrene) matrices as support material

The preparation of transition metal immobilized heterogeneous Lewis acid complex catalysts using 4-vinlypyridine functionlized bead-shaped poly (styrene) as a support material (PSCPVP) have not been largely explored so far. Further, the $TaCl_5$, $MoCl_5$ and $SbCl_5$ Lewis acid or the homogenous form of pyridine based Lewis acid complex catalysts such as Py-$TaCl_5$, Py-$MoCl_5$ and Py-$SbCl_5$ have not been able to attract attention widely due to two reasons. Firstly, the uncomplexed and complexed metal chloride Lewis acid catalysts (soluble) are not environmentally benign; and secondly, these catalysts have not been reused again and as a result, it is considered as expensive, and thus have not been used in large scale industrial reaction. In contrast, if the same metal pentachlorides Lewis acid is complexed with poly(4-vinylpyridine) functionalized bead shaped polymer-supported matrices, then their applications have been potentially enhanced in the preparative procedures. More specifically, we have prepared similar type of three different heterogeneous Lewis acid complex catalysts in the form of microporous beads (mesh –80+100 µm) which can be easily packed into column reactor for continuous mode of reactions.

The three types of heterogeneous Lewis acid complex catalysts were prepared using the following two steps. In the first step, the polymer beads were prepared by adopting the suspension polymerization technique using a modified procedure as described in the experimental section. The resulting poly(styrene) terpolymer beads functionalized with poly(4-vinylpyridine) beads were sieved into different mesh sizes. The representative beads having mesh size viz., –80+100 were analyzed through elemental analysis, FTIR, SEM, EDAX and TGA analysis. All these observed results have been treated as control and thus been compared with each heterogeneous Lewis acid metal complex catalysts.

In the second step, the representative mesh size polymer beads (3 g) were swelled in chloroform and then 10 mmol of Tantalum pentachloride was added and thus obtained $TaCl_5$ immobilized bead-shaped heterogeneous Lewis acid complex catalyst viz., PSCPVP-$TaCl_5$. Similarly, the other two heterogeneous Lewis acid complex catalysts such as PSCPVP-$MoCl_5$ and PSCPVP-$SbCl_5$ were also prepared. The formation of each metal complex catalyst was confirmed by different instrumental techniques which include elemental analysis, FTIR, SEM, EDAX, TGA and DTA and then compared the same with control experimental results.

Elemental analysis

The formation of coordination complex between 4-vinylpyridine substituted PSCPVP beads (matrix) with the respective metal chlorides (Lewis acid) has also been established through elemental analysis. The analysis in terms of % of elements was performed by taking identical weight of plain PSCPVP beads (control) as well as each heterogeneous Lewis acid complex catalyst. The observed elemental analysis results are given in Table 1. The plain terpolymer beads (single unit) i.e., PSCPVP (molecular formula

Table 1 — Comparative relative percentage of C, H and N elements present in each insoluble polymer-supported Lewis acid complex catalysts

Catalyst	Polymer beads						Metal chlorides	
	N (%)		C (%)		H (%)		MCl_5	
	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp
PSCPVP Beads (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
PSCPVP-$MoCl_5$	2.28	2.02	48.85	52.58	4.43	4.99	44.45	40.41
PSCPVP-$SbCl_5$	2.19	1.70	46.88	46.84	4.25	4.50	46.69	46.96

$C_{25}N_1H_{27}$ gives the molecular weight as 341 and thus treated as a control and accordingly theoretical contribution of C, H and N has been calculated in terms of %. On analysis, the plain PSCPVP beads gives 87.93% of Carbon, 8.09% of Hydrogen and 4.10% of Nitrogen and the total of all these elements gives 100%. The values of C, H and N observed are found to agree well with the theoretical values of C, H and N. Hence, we have used these C, H and N values as a base value (control). The immobilization of Lewis acid or soluble metal pentachloride onto the polymeric PSCPVP beads has directly influenced the % of C, H and N in basic values. That is, it is very clear that each metal chloride immobilized heterogeneous Lewis acid catalyst contains C, H, N, Cl and the respective metal atoms. We have determined the individual percentage of C, H and N in each complex catalyst and summed the total percentage, then 100 – total percentage of C, H & N must be the contribution of metal pentachlorides irrespective of heterogeneous Lewis acid catalyst. The percentage of metal chloride calculated by this method has also been compared with their corresponding theoretical values and observed that theoretical value and experimental values have been found to agree well irrespective of metal catalyst. To mention precisely, the comparative study for % of C, H and N between plain PSCPVP matrix and respective metal chlorides immobilized PSCPVP-MCl_5 Lewis acid catalyst has indicated that there has been a sharp reduction in the percentage of C, H and N atoms in each heterogeneous Lewis acid complex catalyst. The sharp reduction of C, H and N noticed in the each complex catalyst has strongly confirmed that in each PSCPVP-MCl_5 catalyst, the respective metal pentachloride has been immobilized and formed a coordination complex of metal Lewis acid catalyst. Based on the observed experimental values of metal chloride in terms of %, we have estimated the moles of metal chlorides immobilized in each polymer complex and studied for comparative catalysis for the esterification reactions.

Fourier transform Infra-red (FTIR) studies

The formation of coordination bond between functionalized 4-vinlyl pyridine and the respective metal chlorides in all the three Lewis acid complex catalysts were established by comparing their respective FTIR (Fig. 3 B-D) and those of the plain PSCPVP beads (Fig. 3A) and individual metal chlorides. On comparison, it is understood from the spectrum that the plain beads give C=N stretching at 1597 cm^{-1} which corresponds to 4-vinylpyridine ring

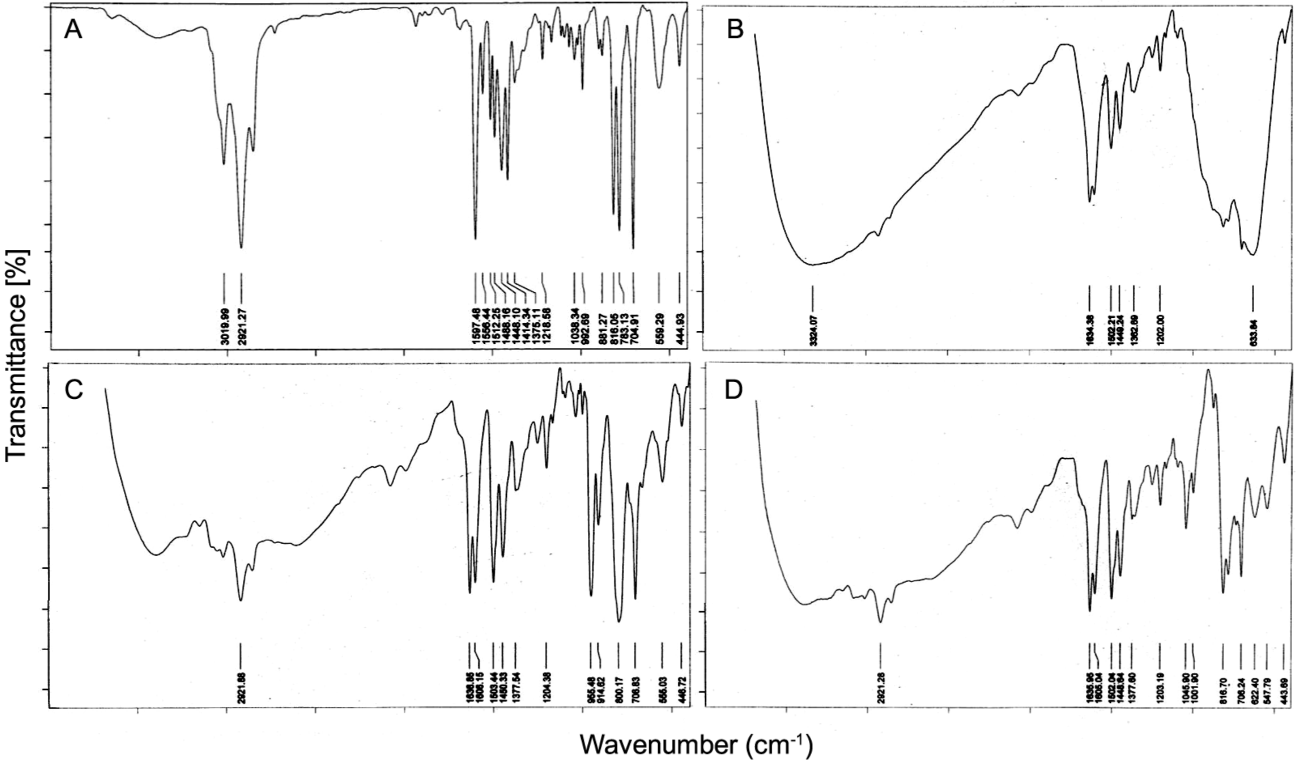


Fig. 3 — FTIR spectra of (A) PSCPVP Beads, (B) PSCPVP-$TaCl_5$, (C) PSCPVP-$MoCl_5$ and (D) PSCPVP-$SbCl_5$

and thus confirmed its functionalization in the PSCPVP matrices. The FTIR spectra of three metal complexes, show new peaks at 1634 cm^{-1} for PSCPVP-$TaCl_5$, 1636 cm^{-1} for PSCPVP-$MoCl_5$ and 1635 cm^{-1} for PSCPVP-$SbCl_5$ (Fig. 3D). These observed new characteristic peaks have not been noticed in the control spectrum of PSCPVP matrix or respective metal chlorides. Thus, the appearance of new peaks in each insoluble complex catalyst has confirmed the formation of coordination bond/complex irrespective of complex catalysts. A similar FTIR observation was reported by Balakrishnan & Murugan[12] for preparation of PSCPVP-$SnCl_4$ catalyst by observing the peak at 1625 and 1630 cm^{-1} for PSCPVP-$ZrCl_4$ and PSCPVP-$TiCl_4$ catalyst, respectively.

Saltykov *et al*.[19] prepared the PVP-$PdCl_2$ and established the formation of co-ordination between poly(vinylpyridine) and $PdCl_2$ through appearance of C=N stretching for pyridine at 1600 cm^{-1} and subsequent shift to 1642 cm^{-1} for Py-$PdCl_2$ complex catalyst and it is due to the deformation of π bonds of pyridine during complex formation. The formation of coordination complex viz., PVP-Cu was also established by Zofia *et al*.[23] through the appearance of C=N stretching at 1600 cm^{-1} and the subsequent shift of vibration mode to 1618 cm^{-1}. That is, the coordination between the unshared electron present in the pyridinic nitrogen atom and the copper metallic centre has lead to form a complex and thus shows the new peak at 1618 cm^{-1}.

Scanning Electron Microscopy (SEM) analysis

The immobilization of Lewis acid moiety viz., $TaCl_5$, $MoCl_5$ and $SbCl_5$ onto cross-linked 4-vinyl-pyridine functionalized poly(styrene) bead matrices has also been studied through change of surface morphology. That is, the surface morphology of the plain beads viz., PSCPVP (Fig. 4A) was compared with surface morphology of the PSCPVP-$TaCl_5$, PSCPVP-$MoCl_5$ and PSCPVP-$SbCl_5$ complex catalysts (Fig. 4 B-D), respectively. On careful comparison with all SEM images, it is observed that the surface morphology of the plain bead was found to be relatively smooth and homogeneous in nature, whereas, the complexed Lewis acid catalysts has shown drastic changes on the surface morphology irrespective of the catalysts. That is, the surface morphology of the overall bead view irrespective of complex catalyst has shown to be heterogeneous, rough and porous in nature. To ensure these observations, we also viewed the single-bead with high resolution irrespective of catalysts and the same has been compared with the single-bead view of plain PSCPVP beads (control). The magnified view of complexed Lewis acid catalyst strongly confirms the changes in the surface morphology when compared with magnified view of plain beads (control). Therefore, the relative change of surface morphology from homogeneous into heterogeneous, rough nodules and porous generation have strongly confirmed the immobilization of respective metal pentachloride through free electron of pyridine nitrogen functionalized in the cross-linked insoluble poly(styrene) matrices. Ruckenstein & Hong[11] had also reported similar type of surface morphology studies for the polymer-supported catalysts. Balakrishnan & Rajendran[21] observed same kind of heterogeneous, nodule formation on the surface of the PSPTC beads. The presence of a number of active sites was also determined from the appearance of tiny nodules on the surface of various insoluble multi-site PS-MPTCs reported by Murugan *et al.*[12].

EDAX Analysis

EDAX is one of the prompt techniques to determine the availability of elements/metals in the complex/catalyst and alloys. The formation of coordination complex between the metal pentachlorides with 4-vinyl pyridine substituted PSCPVP beads has also been confirmed through EDAX analysis. That is, the EDAX spectrum of

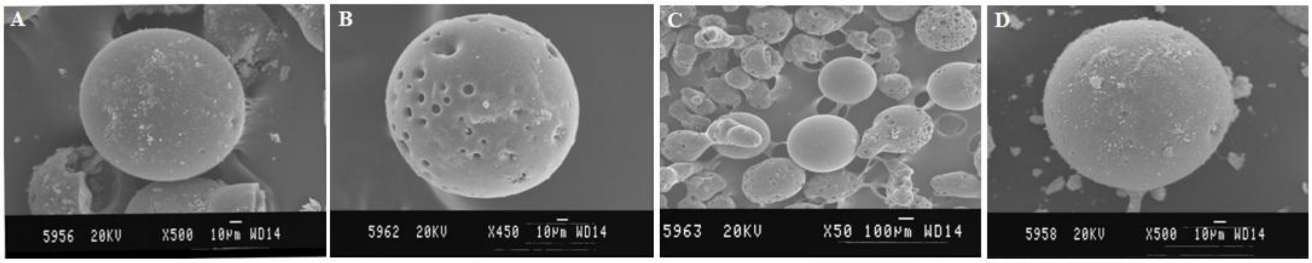


Fig. 4 — SEM images of (A) PSCPVP Beads, (B) PSCPVP-$TaCl_5$, (C) PSCPVP-$MoCl_5$ and (D) PSCPVP-$SbCl_5$

PSCPVP beads (control) was compared with that of PSCPVP-$TaCl_5$, PSCPVP-$MoCl_5$ and PSCPVP-$SbCl_5$ complex catalysts (Fig. 5 A-C) in which it has been noticed that in the control spectrum i.e. PSCPVP there was no characteristic Cl and (or) any of the metal peak. Whereas, it was observed that the Cl peaks appeared in all the spectra irrespective of catalyst as well as peak for Ta, Mo and Sb were also found individually in the corresponding heterogeneous Lewis acid catalyst. These observations strongly indicate the immobilization or formation of coordination complex between respective metal pentachlorides and 4-vinylpyrdine substituted cross-linked poly (styrene) matrices.

Thermogravimetric analyses (TGA)

In TGA analysis, all the three heterogeneous Lewis acid catalysts and PSCPVP beads (control) was heated at controlled rate and then the percentage (%) of weight loss as well as thermal stability was recorded as a function of temperature. From the TGA curves, the thermal stability of the raw beads (control) as well as three different Lewis acid complex catalysts has been ascertained based on the obtained horizontal portion of the TGA. Similarly, the % of weight loss was also determined in all the catalysts along with control beads (PSCPVP).

From the TGA results for PSCPVP beads (control), it is understood that the beads undergo decomposition at three different stages (Fig. 6A). The first decomposition was observed between 180-310°C with 2.3% of weight loss, the second stage was found between 320-480°C with 88% of weight loss. Finally in the third stage, 3% weight loss at 1000-1180°C was observed. This observation reveals that the cross linked 4-vinylpyridine substituted poly (styrene) beads i.e., PSCPVP was decomposed mainly at 320-480°C with weight loss of 88% which was also found to agree well with the earlier reports[21]. The thermogram of PSCPVP-$TaCl_5$ (Fig. 6B) shows that the catalyst has decomposed at five different stages. In the first stage, i.e. between 100 and 180°C, the weight loss occurs at a rate of 13% and the second stage decomposition was noticed between 180-300°C with 5.8% of weight loss; these two different decompositions must be the contribution of moisture and metal chlorides. The large weight loss of (42%) noticed between 290-520°C may be due to the decomposition of polymer matrix. Then, 4.2% and 3.5% weight losses were noticed in the temperature ranges between 520-1100 and 1100-1350°C, respectively and might be the contribution of some charred carbon and oxide impurities. The thermal stability of the catalyst in initial stage decomposition was found to decrease with difference of 80°C as compared with control beads and thus indicate the immobilization of $TaCl_5$ on the polymer matrix.

Similarly, the decomposition pattern of PSCPVP-$MoCl_5$ (Fig. 6C) reveals that the initial decomposition occurs between 80-180°C with weight loss of 10% which way be attributed to the decomposition of moisture and metal chloride ($MoCl_5$). Further, the weight loss of 45 % noticed between 200 to 520°C are pertinent to the decomposition of polymer matrix, 5.3 and 5.6% weight losses noticed in the temperature ranges between 520-1010°C and 1010-1350°C respectively maybe due to impurities in the form of charred carbon and oxides. In the case of thermal decomposition study for PSCPVP-$SbCl_5$ (Fig. 6D) catalyst, it reveals that it undergoes 4 stage decomposition and this pattern and % of weight loss was found to be totally different from other three complex catalysts. That is, in the first step the decomposition was noticed between 90-190°C with

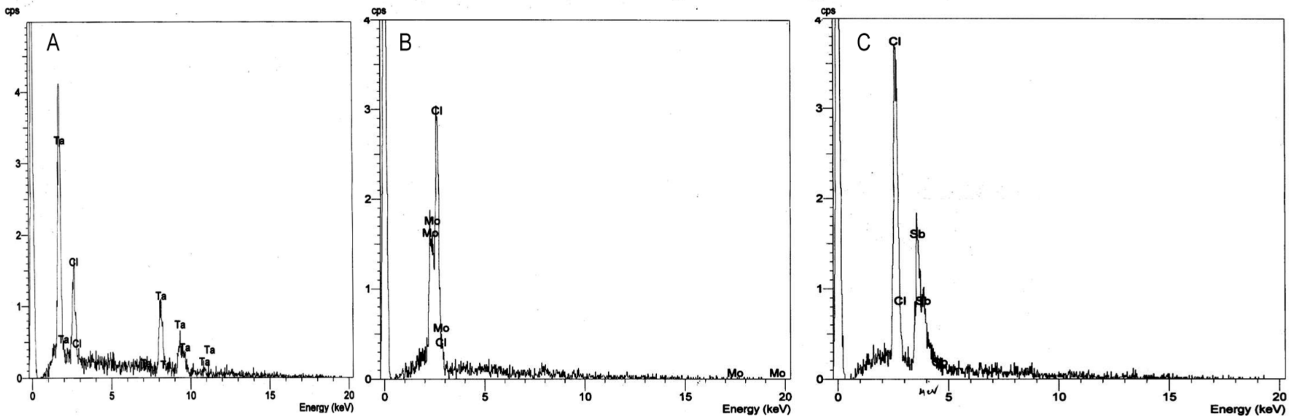


Fig. 5 — EDAX spectra of (A) PSCPVP-$TaCl_5$, (B) PSCPVP-$MoCl_5$ and (C) PSCPVP-$SbCl_5$

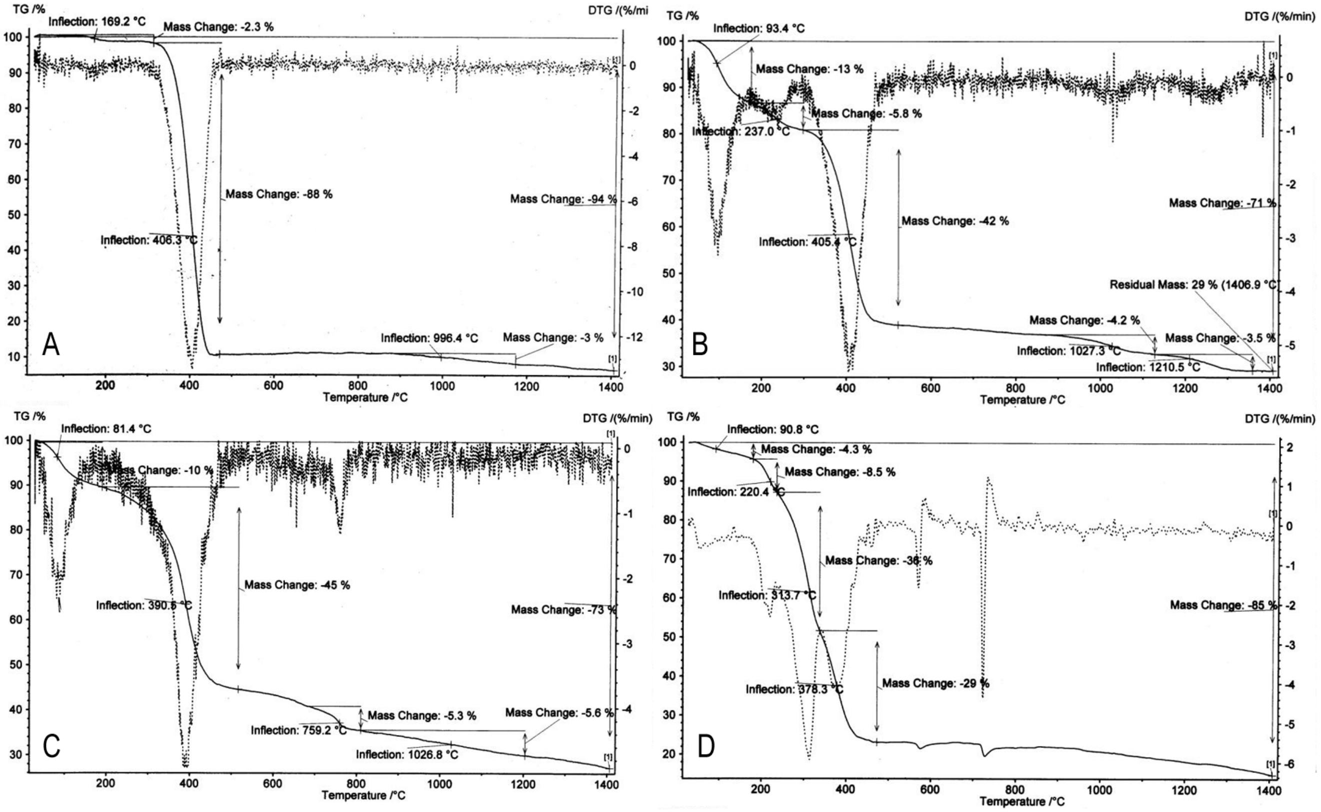


Fig. 6 — TGA thermographs of (A) PSCPVP Beads, (B) PSCPVP-$TaCl_5$, (C) PSCPVP-$MoCl_5$ and (D) PSCPVP-$SbCl_5$

weight loss of 4.3% followed by weight loss of 8.5% in the range 190 to 250°C. As we mentioned earlier, these two different stages of decomposition has been attributed to moisture and chloride. Whereas, the weight loss of 36% noticed between 250-340°C and weight of 29% noticed between 340-480°C are found to be an unusual pattern, which have not been noticed in any of the previous Lewis acid complex catalyst. In fact, as per the control study, 4-vinyl pyridine substituted poly (styrene) matrix (PSCPVP) should decompose between 320-480°C with higher % of weight loss. However, to our surprise, the two stage decomposition obtained between 250-480°C with weight loss of 36 and 29% is found to be little ambiguous to infer and unpredictable. In spite of that, to the best of our knowledge, it is suggested that it must be the decomposition of PSCPVP-$SbCl_5$ immobilized polymer matrix or decomposition of pure Sb and polymer matrix, respectively.

Mahale *et al.*[22] reported thermal studies of seven coordinated Niobium(V) complexes with thiocarbohydraxones. They have explained that the decomposition noticed in the range 60-230°C with a loss of 20.93% was due to the loss of chloride and sulphur, the decomposition continued upto 580°C with weight loss corresponding to the loss of ligand. There was no further weight loss beyond 580°C which indicates the formation of Nb_2O_5. Similarly, Spinelli *et al.*[7] also reported the same type of results in TGA for polymeric cupric complex and compared the same with pure poly (4VP). They have also observed that the thermogram of pure poly (4VP) shows the first weight loss between 80 to 100°C and this is due to the presence of water. A second and total weight loss occurs at 400 to 470°C and this was ascertained as 4-vinly pyridine substituted polymer film. The cupric based SCN immobilized 4-vinyl-pyridine complex has sharply reduced the decomposition temperature from 400°C to 200°C. From this inference, the authors have suggested that the metal complex immobilized polymeric material was always thermally less stable than the original poly(4-vinylpyridine) polymer. Similarly, Michalska & Strzelec[23] had synthesized polymer-supported rhodium catalysts using polyamide supports substituted with pyridine moiety, in which they also proved that the plain polyamide support material was found to be thermally more stable than the Rh immobilized polymer-supported catalyst.

Comparative study for efficiency of various soluble Lewis acid metal complex catalysts for esterification

Although the results of spectroscopy, microscopy and TGA analyses for homogenous and heterogeneous Lewis acid complex catalysts have concretely proved the formation of complex between pyridine with metal chloride in the case of homogenous catalyst and between 4-vinylpyridine substituted poly (styrene) matrix (PSCPVP) with different metal chlorides in the case a of heterogeneous catalyst, but when they are used to conduct the reactions, sometimes they behaved differently in reaction medium. Hence, the catalytic efficiency of six different types of catalysts including three different soluble catalysts viz., Py-$TaCl_5$, Py-$MoCl_5$ and Py-$SbCl_5$ and 3 different insoluble catalysts viz., PSCPVP-$TaCl_5$, PSCPVP-$MoCl_5$ and PSCPVP-$SbCl_5$ were examined by conducting the comparative study using esterification of acetic acid with butanol. Esterification reaction was studied under pseudo-first order conditions using 0.25 mmol soluble catalyst and 0.5 mmol of insoluble catalyst. The performances of these catalysts i.e., among the homogenous catalysts as well as among the heterogeneous catalysts, were assessed based on their pseudo-first order rate constants. The obtained rate constants are presented in Tables 2 & 3, respectively.

From the comparative catalytic activity in esterification reaction (Table 2), the relative order among the homogenous Lewis acid catalysts is observed as Py-$TaCl_5$> Py-$MoCl_5$> Py-$SbCl_5$. From the k_{obs} values, it is proved that all the three homogeneous catalysts are capable of accelerating esterification reaction. Further, the order of reactivity among the catalyst usually depends on the (i) order of Lewis acidity of the catalyst, (ii) nature of the reaction or reactant and (iii) Medium. Whereas, the difference in catalyst activity found in esterification may be attributed mainly to the electrophilicity of catalyst-reactant complex formed and the degree of Lewis acidity. In other words, it also depends on the degree of electrostatic interaction between unshared electrons of pyridine with metal chloride, the geometry of the metal complex catalyst, stability of the complex and the coordination strength between metal chloride and pyridine ligands. Furthermore, the nature of the reactant had also contributed in the reaction yield, particularly in terms of size and possible orientation of substrate attraction towards the Lewis acidity of the complex catalyst. In the case of medium, the polarity of the solvent is usually the influential factor in any chemical reaction.

Table 2 — Comparative catalytic efficiency of 3 different types of soluble Lewis acid metal complex catalysts for esterification of acetic acid with butanol

S. No.	Name of the catalyst	$k_{obs}\times10^3$ (min^{-1})
1	Py- $TaCl_5$	7.26
2	Py- $MoCl_5$	5.48
3	Py- $SbCl_5$	1.47

[Butanol: 10.93 mmol (1 mL); Stirring speed: 400 rpm; Acetic acid: 524.6 mmol (30 mL); Temp.: 30ºC±0.1; Insoluble Catalyst: 0.5 mmol]

Table 3 — Comparative catalytic efficiency of 3 different types of Insoluble Lewis acid metal complex catalysts for esterification of acetic acid with butanol

S. No.	Catalyst	$k_{obs}\times10^3$ (min^{-1})
1	PSCPVP- $TaCl_5$	5.18
2	PSCPVP- $MoCl_5$	2.24
3	PSCPVP- $SbCl_5$	0.87

[Butanol: 10.93 mmol (1 mL); Stirring speed: 400 rpm; Acetic acid: 524.6 mmol (30 mL); Temp.: 30ºC±0.1; Insoluble Catalyst: 0.5 mmol]

The lower activity observed in the present study of Py-$MoCl_5$ and Py-$SbCl_5$ complex catalysts in esterification reaction may be mainly due to the lower stability of the complex. Particularly, the least catalytic activity noticed in the Py-$SbCl_5$ complex is attributed to the following reasons. That is, $SbCl_5$ is usually very volatile and corrosive; more importantly, antimony can be easily reduced from Sb^V to Sb^{III} even in room temperature. Further, we also believe that since $SbCl_5$ is highly volatile in nature, while adding the $SbCl_5$ for Py-$SbCl_5$ preparation, partial amount of $SbCl_5$ might have escaped and thus only lower concentration of $SbCl_5$ involved as a complex with pyridine ligand and hence decrease in the Lewis acidity. Therefore, the high volatile nature of $SbCl_5$, free reduction of Sb^V to Sb^{III} and thereby reduced the complex stability are observed to be the main reasons for the lower Lewis acidity which in turn reflected in the least catalytic activity in esterification reaction compared with other soluble catalysts. In fact, Salome *et al.*[24] compared the activity of various Lewis acids in the liquid phase fluorination of trichloro methoxy-benzene by HF in which they proved that only the Lewis acids with an oxidation state of +V like $MoCl_5$, $TaCl_5$ and $SbCl_5$ allows the least Cl/F exchange and especially $MoCl_5$ are still reduced the Cl/F exchange among all.

Similarly, in the case of Py-$MoCl_5$ complex, the $MoCl_5$ is so hygroscopic and hence it reacts instantly with atmospheric moisture even at room temperature and forms $MoCl_3$ and that leads to the reduced stability of the complex. To believe this fact, it is also learnt from the literature that there is a possibility of decomposition of $MoCl_5$ and leads to liberate the Cl_2 gas and hence reduced the stability of the complex. In contrast, similar decomposition or lower stability of the complex is not found in the case of $TaCl_5$. In other words, the thermodynamic stability of the Py-$MoCl_5$ and Py-$SbCl_5$ complex was proved to be less and hence when these two catalysts were employed in the esterification. After sometime, the Lewis acidity of the complex may be reduced gradually and thus reflected in the lower activity, whereas, the Py-$TaCl_5$ was found to be relatively more stable than the Py-$MoCl_5$ and Py-$SbCl_5$ complex catalysts.

However, among all the three complexed catalysts, Py-$TaCl_5$ complexes are more stable than others as $TaCl_5$ is more resistant to reduction, Ekstrom *et al.*[25] proved that Ta was more stable than Nb in the stabilization of complex with open structures. Grasselli *et al.*[26] also studied the catalytic behavior of Ta and Nb based catalysts in the ammoxidation of propane and found that Ta based catalyst is more stable than Nb.

Therefore, although the order of activity among the homogeneous Lewis acid complex catalysts depends on various factors including the geometry of the complex, coordination number of the metal, medium, temperature, structure of the reactant and possible attraction/orientation of substrate towards Lewis acidity of the complex. But, we have mainly highlighted our explanation that the order of reactivity of complex catalyst depends on stability of the complex. Secondly, the, higher activity observed in Py-$TaCl_5$ than with Py-$MoCl_5$ and Py-$SbCl_5$ are also due to their higher degree of oxophilic attraction. That is, tantalum is highly oxophilic in nature and hence apart from the Lewis acidity of the catalyst, this metal complex can freely attract the oxygen molecule present in the substrate i.e., -CH_2OH of butyl alcohol and -COOH group of acetic acid due to exophilic attraction and hence these two substrates would reach the acidic site of the metal complex very effectively or they come closer, and hence the reaction would proceed fastly and gives higher rate constant. Similar type of study has already been reported by Kee *et al.*[18]. Similarly, it was concluded that the reason for higher yield is the higher covalent coordination power of observation has already been reported in which $MoCl_5$ based catalysts are effective for polymerization of acetylene derivatives, especially those containing oxygen molecule, such as propiolic acid, dipropargyl ether and dipropargyl carbinols. Guo *et al.*[27] also reported the comparative catalytic activity of group V and VI metal chlorides ($MoCl_5$, WCl_6, $NbCl_5$, $TaCl_5$) with conventional Lewis acid catalysts such as $ZnCl_2$, $AlCl_3$, $SnCl_4$ and $TiCl_4$ for C-O bond cleavage of dibutyl ether with benzoyl chloride and found that the group V and 1V metal chlorides showed better results than the conventional ones. They also demonstrated that among the group V and VI metal chlorides, $MoCl_5$ was found to be an efficient catalyst on comparison with $TaCl_5$, $NbCl_5$ and WCl_6, because the C-O groups can interact with transition metal centre (Mo) through their π-electrons very effectively. Similarly, in the present study also, the Py-$MoCl_5$ complex catalyst can easily react with acetic anhydride and alcohol than with Py-$TaCl_5$ and Py-$NbCl_5$ catalyst. Because, as mentioned in the literature, the high covalent coordination power of molybdenum pentachloride complex and its quick formation of transition complex with acetic anhydride and alcohol due to intensive oxophilic character that would facilitate the reaction more effectively than with the $TaCl_5$ coordinated catalysts.

Therefore, in a nutshell, in the earlier studies, although the catalytic activity of Lewis acid complex was explained mainly with geometry of the complex, and corresponding Lewis acidity but in our study, we have offered our explanation based on the thermal stability of the complex and oxophilic character of the substrates with respect to metal chlorides. Hence, as far as soluble Lewis acid catalyst is concerned, Py-$TaCl_5$ is found to be more stable than any other complex catalyst that is reflected in the increased order of rate constant in esterification.

Is PSCPVP-MCl_5 stable and reusable?

The very purpose of immobilizing the less stable Lewis acids viz., transition metal based pentachlorides, such as $TaCl_5$ & $MoCl_5$ and non-transition metal pentachloride viz., $SbCl_5$ onto the bead-shaped cross-linked PSCPVP matrix via coordination complex was aimed at various objectives. That is, the first and foremost objective is to develop the convenient and stable Lewis acid complex (or) to enhance the reusability/increase the recycle number, higher selectivity, easier handling, simple work-up procedures, non-toxicity, non-corrosiveness and mildness of the reaction condition. Above all, the developed bead-shaped heterogeneous Lewis acid catalysts can easily be packed in column reactor and thus leads to conduct the esterification reactions in continuous mode operation and hence pave a way for larger/industrial scale production of esters. Most importantly, easy recovery and reusability with consistent activity have been the utmost objective of this study. The reusability of catalyst used to depend on stability of the complex.

Although, all the bead-shaped insoluble heterogeneous Lewis acid complex catalysts have proved to accelerate the esterification reaction effectively in the first cycle, but in order to determine the stability of complex, it is a must and logical to examine the reactivity in the second and subsequent cycles also. Because, sometimes the added Lewis acid metal chloride MCl_5 may physically entrapped onto the PSCPVP matrix without forming the co-ordination complex with unshared electrons of 4-vinylpyridine substituted in PSCPVP and this in turn would easily leach out the metal chlorides (MCl_5) in the first cycle itself and thus have the possibility for reduction in catalyst activity.

Therefore, in order to exclude the possibility of leachability or physisorption or physical entrapment of MCl_5 onto the PSCPVP matrix, we decided to reuse the catalyst for another two cycles (excluding the first cycle) irrespective of metal chlorides for esterification of acetic acid with butanol reaction by adopting the identical experimental conditions as it was followed in the respective first cycle catalyst condition. The observed pseudo-first order rate constants are given in Table 4. From the obtained k_{obs}, it is suggested that the efficiency of PSCPVP-$MoCl_5$ and PSCPVP-$SbCl_5$ are found to decline sharply even in second cycle, thus proving the poor stability of complex or leachability of the metal pentachlorides. Particularly, the $SbCl_5$ immobilized complex is found to be not active even in third cycle.

This observation certainly confirmed that $SbCl_5$ undergoes reduction and gives lower state (Sb^V to Sb^{III}) complex. In the case of $MoCl_5$ it was also found to be lower stability because of facile possibility of decomposability by the liberation of chloride gas (Cl_2). Hence, these two catalysts are unsuitable to reuse again. In contrast, the PSCPVP-$TaCl_5$ Lewis acid complex catalyst was found to maintain their catalytic activity even up to third cycle with negligible reduction as compared with the first cycle activity. Therefore, the possibility of physisorption or physical entrapment of MCl_5 or leachability of MCl_5 from PSCPVP matrix has been completely ruled out, because, if MCl_5 is physisorbed or entrapped onto the matrix, then they may easily leach out from the matrix during the stirring of reaction even at the first cycle itself. Whereas, the consistency in activity at the second and third cycle has unambiguously proved that $TaCl_5$ have formed a stable coordination bond with lone-pair of electrons in pyridine N atom substituted in the PSCPVP matrix and thus confirmed the stability of the respective Lewis acid complex.

Table 4 — Comparative recycling efficiency of insoluble PSCPVP-MCl_5 catalysts for esterification of acetic acid with butanol

No. of cycles	$k_{obs}x10^3$ (min^{-1})		
	PSCPVP-$TaCl_5$	PSCPVP-$MoCl_5$	PSCPVP-$SbCl_5$
1	5.18	2.24	0.87
2	4.80	0.87	0.26
3	4.60	0.23	-

[Butanol: 10.93 mmol (1 mL); Stirring speed: 400 rpm; Acetic acid: 524.6 mmol (30 mL); Temp.: 30ºC±0.1; Insoluble Catalyst: 0.5 mmol]

Conclusions

In summary, we have developed three different types of soluble and three different types of convenient bead-shaped micro porous PSCPVP-MCl_5 (M= Ta, Mo & Sb) Lewis acid complex catalysts which in turn actively accelerate both the esterification reactions. All the six catalysts were characterized by FTIR, SEM, EDAX, CHN and TGA analyses. The comparative catalytic efficiency of the soluble and insoluble catalysts was assessed based on ascertaining the pseudo-first order rate constants. That is, the comparative study was carried out, by determining the rate constants among the soluble catalysts viz., Py-$TaCl_5$, Py-$MoCl_5$ and Py-$SbCl_5$ as well as among the insoluble catalysts such as PSCPVP-$TaCl_5$, PSCPVP-$MoCl_5$ and PSCPVP-$SbCl_5$ for esterification reaction of acetic acid with n-butanol. The order of reactivity among the three soluble catalysts in esterification is as follows, Py-$TaCl_5$ > Py-$MoCl_5$ > Py-$SbCl_5$.. The reasons for obtaining this kind of order has been mainly explained based on stability of the complex and oxophilic attraction. Similarly, among the three different insoluble catalysts, the order of reactivity in esterification is as follows, PSCPVP-$TaCl_5$ > PSCPVP-$MoCl_5$ > PSCPVP-$SbCl_5$ and the reasons for obtaining a lower/higher catalytic activity are explained based on the polymeric support and stability of the complex. The catalytic activity of soluble Py-$TaCl_5$, Py-$MoCl_5$, Py-$SbCl_5$ catalyst was found to be 1.40, 2.44 and 1.68 fold times more active than PSCPVP-$TaCl_5$, PSCPVP-$MoCl_5$ and PSCPVP-

$SbCl_5$, respectively for esterification reaction. In case of declining in activity of insoluble catalysts after some cycles, they can be easily regenerated by simple treatment with respective metal chlorides i.e. by simple stirring of MCl_5 with swelled PSCPVP bead matrix and thus certainly possible to get the original activity. These beads can be employed to be packed in the column reactor for continuous mode operation or industrial scale operation.

Conflict of interest

The authors declare no conflict of interests in this study.

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