



Designing efficient metal complex catalysts for acylation: A comparative study with soluble and insoluble catalysts systems

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New soluble and insoluble Nb, Ta, Mo, and Sb complex catalysts have been developed using pyridine and polymer-supported cross-linked (poly-4-vinyl pyridine) bead (PSCPVP), and characterized using FT-IR, SEM, EDAX, elemental analysis (CHN), and TGA. Their ability to catalyze the acylation of ethanol with acetic anhydride at 303K has been proven. Both soluble and insoluble chemicals have the same order of activity: MoCl_5 , TaCl_5 , NbCl_5 , and SbCl_5 . The insoluble catalyst outperformed in terms of activity by complex catalysts, although they have significant limitations in terms of solubility and recyclability and soluble homogeneous catalysts in terms of lowest cost and recyclability, whereas all soluble Py-MCl_5 catalysts exhibit better activity than insoluble PSCPVP- MCl_5 catalysts according to the computed k_{obs} values. Insoluble catalysts are preferable than soluble homogeneous catalysts in terms of recyclability, although all the soluble catalysts of Py-MCl_5 , $\text{M} = \text{Nb, Ta, Mo, and Sb}$ have exhibited better activity than insoluble PSCPVP- MCl_5 ($k_{\text{obs}} = 6.51, 6.98, 7.48 \text{ \& } 1.73 \times 10^3 \text{ min}^{-1}$) based on the computed k_{obs} values. For acylation process, it has been found that the soluble Py-NbCl_5 , Py-TaCl_5 , Py-MoCl_5 , and Py-SbCl_5 catalysts whereas 1.47, 1.63, 1.59, and 1.67 folds more active than PSCPVP- NbCl_5 , PSCPVP- TaCl_5 , PSCPVP- MoCl_5 , and PSCPVP- SbCl_5 correspondingly.

Keywords: Antimony pentachloride, Insoluble catalysts, Molybdenum pentachloride, Niobium pentachloride, Tantalum pentachloride

Catalysts are substances that cause a change in the rate of a chemical reaction without themselves being consumed in the reaction. Catalysts are often divided into two main types Homogenous and heterogeneous. Compared to homogenous catalysts, heterogeneous catalysts would be more useful for industrial applications. Generally, heterogeneous are prepared by the immobilization or anchoring of the active catalytic site onto the inorganic /polymeric matrix. Specifically, the insoluble bead-shaped polymer-supported catalyst is an industrially important compound due to its uncomplicated handling and reusability via simple filtration. Further immobilization of metal active-site onto organic matrices has been considered as a greener catalytic material to perform valuable organic transformations in single/biphasic medium, particularly for industrially important reactions including esterification¹, acylation², and Ketalization reactions. The favoured organic polymers that are frequently used as supports include poly(styrene), poly(propylene), poly(acrylates), and poly (vinyl chloride). These polymers specially offer several advantages over other supports viz. (i) they are easily functionalized, (ii) Most

of the hydrocarbon polymers are chemically inert and as a result, it does not interfere with the catalytic group, and (iii) Polymers are often prepared with a wide range of physical properties and hence their porosity, surface area, and solution characteristic are also often altered by varying the degree of cross-linking. Thus, poly(styrene), which is far and away the most widely used polymer variation in the degree of cross linking, allows an almost continual change from essentially a soluble material (2% cross-linking polystyrene) to a totally insoluble material at 20 % cross-linking polystyrene with in the preparation of polymer-supported metal complex catalysts. Several functional polymers are reported in the literature for the preparation of polymer-supported reagents and catalysts and the same is used in the acylation and alkylation of different substrates. The insoluble polymer catalyst containing the anhydride functional group was used for the conversion of amine or alcohol to amide or ester^{3,4}. Most of the supports used thus far for the preparation of polymer-supported transition metal-based Lewis's acids are found to be functional organic polymers. Among these polymers the nitrogen-

containing molecules have received considerable attention due to their complexing ability and stability to thermal oxidation. The polyamide pyridine moiety immobilized metal species are found to be highly active and selective catalysts for organic reactions. The polymer-supported transition metal catalysts and their applications are of greater importance for industrial processes⁵⁻⁹. Organometallic complexes used as catalysts are very expensive but losses during the utilization of polymer-supported catalysts are minimized¹⁰. Attaching the catalyst to the polymer backbone leads to an increase in the steric environment of the catalyst. As an outcome of this restriction around the catalyst center, substrate selectivity is increased.

The Lewis acids are well-known acid catalysts used frequently to enhance the yield in any related organic transformation reactions. Lewis acids like TaCl_5 ¹¹, $\text{Se}(\text{OTf})_3$ ¹², and $\text{Cu}(\text{OTf})_2$ ¹³ have also been used as catalysts for the acylation of alcohols and amines with acyl anhydrides. Acyl halide or metals in the polymer or by interaction with the functional group of resin¹⁴⁻¹⁸. A polystyrene resin with aluminium trichloride employing a suitable solvent produces a tightly bound complex of insoluble polymer and anhydrous Lewis's acid on removal of the solvent¹⁹. The polymer-supported Lewis acid is quickly made available by swelling the resin with an appropriate solvent, which within the dry state, the acid is shielded from hydrolysis. Balakrishnan *et al.*²⁰ described that though titanium tetrachloride has many advantages in homogenous conditions, its predominant drawbacks such as its corrosive nature, difficulties in separation and recovery/reuse result in the large volumes of environmentally hazardous waste associated with its use. Acylation of alcohols and phenols is a crucial and routinely utilized transformation in organic synthesis. Acyl anhydrides have been commonly used reagents in the presence of an acid or catalyst for acylation reactions. Similarly, within the preparation of acetates, the utilization of acetic acid or acetic anhydride and pyridine is the most commonly used reagents. In recent years various primary, secondary, benzylic, and cyclic alcohols and phenols were subjected to acylation in appreciable yields. In acylation reaction study exploitation of environmentally friendly heterogeneous catalyst to perform the reaction for larger scale are developed nowadays.

Murugan, *et al.*, Proposed highly sensitive, stable G-CN decorated with Ag NPs for SERS sensing of toluidine blue and catalytic reduction of crystal

violet²¹. Murugan, *et al.*, have implemented hydrothermal synthesis, characterization and electrochemical behavior of NiMoO_4 nanoflower and $\text{NiMoO}_4/\text{rGO}$ nanocomposite for high-performance supercapacitors²². Santhoshkumar S and Murugan E have discussed about size controlled silver nanoparticles on β -cyclodextrin/graphitic carbon nitride: an excellent nanohybrid material for SERS and catalytic applications²³⁻³¹. As far as we know, the study of metal Penta chloride catalyzed acylation of acetic anhydride with ethanol was not reported in the associated academic literature. This study focuses on development of soluble catalysts from pyridine and insoluble catalysts with polymer beads using Niobium pentachloride, Tantalum pentachloride, Molybdenum pentachloride and Antimony pentachloride by acylation reaction.

Experimental Section

Materials

Styrene, 4-vinyl pyridine, polyvinyl alcohol and divinylbenzene from Fluka were utilized as such. Ethanol, AIBN (Koch-light, USA) was recrystallized. Gelatin (BDH), boric acid, acetic acid and NbCl_5 (Merck), NaOH and NaNO_2 (SRL), TaCl_5 (Lancaster), MoCl_5 and SbCl_5 (Sterm), chloroform, methanol, acetone, acetic anhydride, and ethanol were all purified.

Synthesis of soluble Py- MCl_5 Lewis acid catalyst

Pyridine 20 mmol were dissolved in 100 mL of chloroform and placed in a 150 mL single-necked RB flask. Niobium, Tantalum, Molybdenum, and antimony pentachloride (20 mmol) were carefully added to this homogeneous solution using a fuming cupboard. A magnetic stirrer was used to agitate the reaction mixture in the flask for one hour at room temperature. The resultant soluble Py- MCl_5 Lewis acid complex catalyst was filtered under vacuum and repeatedly chloroform washed (3×100 mL). As the resulting Py- MCl_5 complex catalyst is hygroscopic by nature, it was kept in a vacuum desiccator for storage. Yields for Py- NbCl_5 , Py- TaCl_5 , Py- MoCl_5 , and Py- SbCl_5 are respectively 58.9%, 60%, 48%, and 35% (Scheme 1).

Synthesis of polymer PSCPVP beads

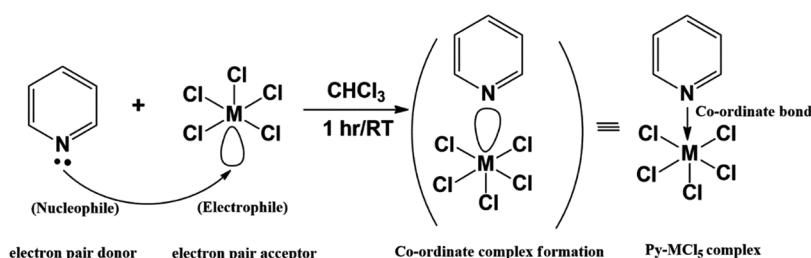
The insoluble polymer-supported cross-linked poly (4-vinyl pyridine) (PSCPVP) beads were created by following the first method in literature³². Styrene (supporting), divinyl benzene (crosslinking), and 4-vinyl pyridine (functional) monomers are co-

polymerized in suspension in this strategy. The organic phase was kept at 82.5 g, and the aqueous phase was kept at 225 g by fixing 25% active site and 2 percentage crosslinking (ratio of 4-VP and DVB). In 30, 60, and 130 mL of double distilled hot water, respectively, 1.35 g of gelatin, 2.55 g of boric acid, and 2.25 g of polyvinyl alcohol were fully dissolved (50°C). The medium was highly viscous hence the temperature was maintained at 50°C. The temperature was further increased to 70°C decompose AIBN dissolve completely. The pH maintained is 10 to avoid transfer of 4 vinyl pyridine by protonation. The medium's viscosity was preserved by the polyvinyl alcohol that has been dissolved. Then, at 30 degrees Celsius, these solutions were combined. To keep the gelatin in its original shape, 0.1 g of sodium nitrite was added after the pH of the combined solution was brought down to 10 by the addition of 25% aqueous caustic soda solution. Only after bringing the pH to 10 did the aqueous phase become transparent. It was then transferred to a 250 mL three-necked RB flask that had a reflux condenser and an overhead mechanical stirrer. Since nitrogen was continually passed, a temperature of 50°C was maintained. The organic phase, which contained 3.3 g of DVB, 58.52 g of styrene, 25.76 g of 4-vinyl pyridine, and 0.4125 g of AIBN, was properly mixed and introduced to the reaction flask after 30 min (while keeping the aforementioned conditions). The stirrer's blade level

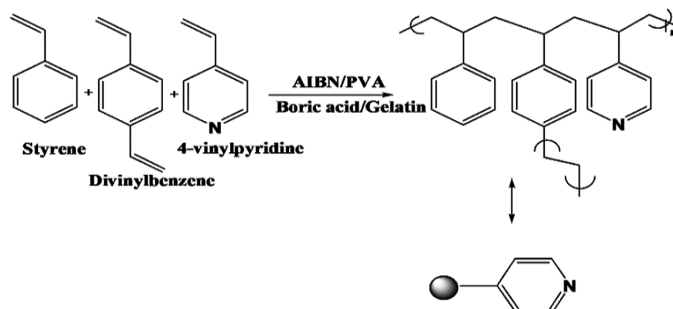
was changed to position the tips in the organic phase and the majority of the blades in the aqueous phase. The thermostat temperature was then raised to 70°C, and a tachometer was used to keep the stirring speed constant at 400 rpm. The polymerization process was let to run for 48 h (Scheme 2). In order to prevent the wash solution from becoming hazy when water was added, the resultant polymer beads were repeatedly washed with hot water and cold methanol via a Buckner funnel. The material was then dried for two days in a vacuum oven set at 60°C, resulting in the production of insoluble crosslinked copolymer PSCPVP beads. The polymer beads were then sieved using a RO-TAP testing Sieve Shaker (W.S. Tyler Company, Cleveland, Ohio), yielding various particle sizes, including -60 + 80, -80 + 100, -120 + 170, -170 + 300 and over -300 mesh.

Immobilization of MCl_5 on to the PSCPVP beads

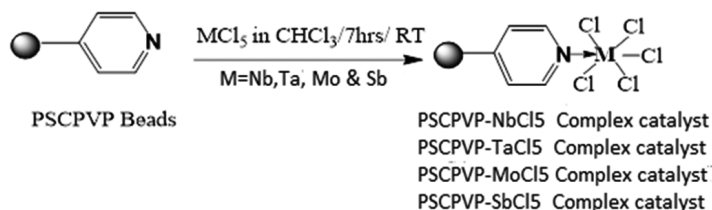
In a 150 mL RB flask equipped with a guard tube containing anhydrous calcium chloride and to which 10 mmol of metal pentachloride was added³³⁻³⁸, the insoluble PSCPVP beads (3 g) were swollen in chloroform (100 mL) for 1 h. the polymer-supported (4-vinyl pyridine)-niobium pentachloride complex Lewis's acid catalyst (PSCPVP- MCl_5), which was filtered and then washed with chloroform and acetone to remove the unreacted MCl_5 . the resulting reaction mixture was stirred for 7 h at room temperature and then cooled to 0-10°C. The PSCPVP- MCl_5 catalyst



Scheme 1 — Synthesis of soluble Py- MCl_5 Lewis acid catalyst (M= Nb, Ta, Mo and Sb)



Scheme 2 — Preparation of PSCPVP beads.

Scheme 3 —Immobilization with MCl₅ on PSCPVP beads.

was then dried for a further 24 h at 50°C under vacuum. Scheme 3 describes how to make the PSCPVP-MCl₅ complex catalyst.

Characterization techniques

The Bruker Tensor-27 FT-IR spectrophotometer with OPUS software was used to record all FT-IR spectra. The background calibrations were performed using a pure KBr pellet, and the sampling was completed using KBr pellets containing the required amount of sample. On a Techomp 8500 equipment, UV-Vis spectra were measured using UV-Vis analyzer software. The sample analysis was carried out while keeping a wavelength range of 200 nm to 800 nm. ElementarVario EL III CHN Analyzer was used to conduct the CHN analysis. HITACHI S-3000H was used to capture SEM pictures. Operating at various electron voltages and at various distances was the scanning electron microscope. After the metal stub was given time to scan, a strip of double-sided conducting carbon tape was attached, and the samples were subsequently put to the carbon tape. SEM analysis was done on PSCPVP-NbCl₅, a polymer-supported metal complex catalyst with a mesh size of +80-100, and it was compared to plain PSCPVP beads with the same mesh size. Polymeric metal complex catalysts should be coated with gold to make them conductive since they are electrically non-conducting. On the surface of double-sided tape, one side of which was previously affixed to the surface of a circular copper disc pivoting on a rod, the corresponding complicated catalysts were spread out. The gold coating was applied using an HITACHI S-3000H auto fine-coating ion sputter under the same experimental setup. A ZETSCHE STA 409C thermal analyzer was used to complete the thermogravimetric studies.

Acylation of ethanol with acetic anhydride using soluble and insoluble Lewis's acid complex catalyst

By carrying out the acylation of ethanol with acetic anhydride (excess) under comparable experimental

circumstances and by adhering to the pseudo-first-order kinetics, the comparative catalytic efficacy of 4 distinct soluble Lewis's acid complex catalysts was further independently validated. Here, the typical acylation process has been laid out. In other words, 1 mL of ethanol (17.06 mmol) and 30 mL (317.4 mmol) of acetic anhydride were added to a 150 mL two-necked round bottom flask. The flask was once again placed under a thermostat set at 30°C and agitated for 10 min at 400 rpm to condition the substrates before adding the catalyst. The reaction mixture's reaction mixture was sampled (zero time). The reaction was then allowed to continue after 0.25 mmol of each of the soluble Lewis acid metal complex catalysts was added separately to the reaction mixture. Every 5 min, samples of every catalysed reaction were taken and evaluated using GC at regular intervals of time. Following the pseudo-first-order kinetics of the process, a gas chromatograph was used to calculate how much ethanol vanished. The 5% Chrom WHP 80/100, 3 m × 1/8" stainless steel column used for the analysis was flowed through at a rate of 30 mL/min using nitrogen as the carrier gas. The temperature of the column oven was held constant for 3 min (60 °C) following the injection of the samples, then raised linearly to 160°C (30°C min⁻¹), and maintained at this temperature for the duration of the research. Temperatures for the injector and detector were set at 250 and 270°C, respectively. A Hamilton micro syringe was used to inject 0.5 mL of the reaction mixture onto the column for each sample, and the result was then examined. The retention times for ethanol were 1.47 min, acetic anhydride was 4.21 min, and the acylated product was noted at 1.37 min. The decline in ethanol concentration over time and the plots of log (a-x) vs time, where (a-x) denotes the concentration of ethanol at a certain time 't', were used to determine the pseudo-first-order rate constants. Table 1 lists the derived comparative pseudo-first-order rate constants without taking into account the soluble Lewis acid catalysts. Similar to the comparison study of acylation of ethanol with acetic anhydride described above, PSCPVP-NbCl₅,

PSCPVP-TaCl₅, PSCPVP-MoCl₅, and PSCPVP-SbCl₅ were used as the 4 different insoluble polymer-supported crosslinked poly (4-vinyl pyridine)-Lewis acid catalysts under identical pseudo-first order experimental conditions. The only difference was the amount of the respective catalyst used (0.5 mmol). Table 2 contains the estimated comparative pseudo-first-order rate constants, which are independent of the catalysts used in 4 distinct insoluble reactions. (Scheme 4). Since the entire work was based on kinetics the conversion of reactant is not mentioned in the manuscript. We only monitor the concentration of the reactant by GC which is essential for obtaining kinetics

Reusability and recycling of the catalyst

These 4 distinct polymer-supported Lewis acid complex catalysts have each had their stability and catalytic activity evaluated separately since, occasionally, the catalytic activity was somewhat reduced due to the deterioration or leaching of metal chlorides. Since they were employed in the first cycle, the corresponding polymer-supported metal complex catalysts have been recovered using filtering, washed with methanol/acetone, and then dried. The acylation of ethanol was then carried out using each of the independent metal complex Lewis acid catalysts under the same pseudo-first-order conditions as the first cycle. In other words, the reusability of four different insoluble polymer-supported metal complex

catalysts—PSCPVP-NbCl₅, PSCPVP-TaCl₅, PSCPVP-MoCl₅, and PSCPVP-SbCl₅—was examined separately by carrying out the same esterification of acetic acid with butanol reactions under the same first cycle pseudo-first order experimental conditions.

Result and Discussion

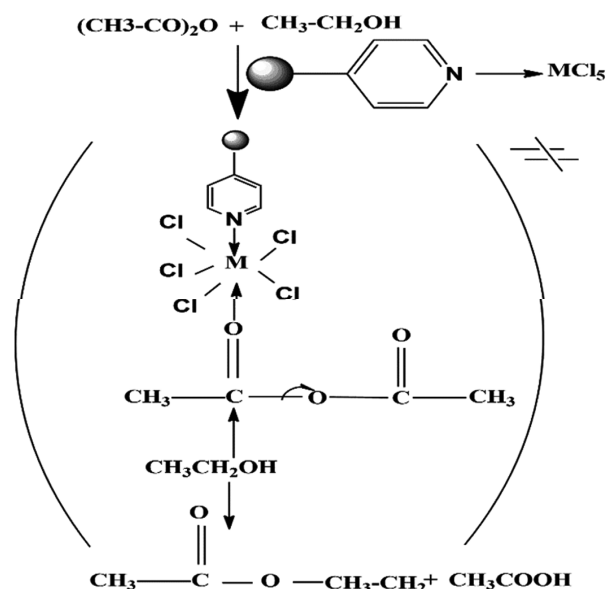
With the use of FT-IR, elemental analysis, SEM, EDAX, and TGA, the PSCPVP beads were identified. PSCPVP is a cross linked polymer and hence arrangement of polymer chain to form crystal lattices will be difficult. So, X-ray diffraction analysis is not necessary for cross linked polymer. Fig 1(a-e) shows the FT-IR spectrum of the PSCPVP-NbCl₅, PSCPVP-TaCl₅, PSCPVP-MoCl₅, PSCPVP-SbCl₅, and PSCPVP beads. Due to C=N stretching, the poly-4-vinylpyridine IR spectra exhibit an absorption band at 1600 cm⁻¹. A novel absorption band for PSCPVP-MCl₅ at 1634 cm⁻¹. The Py-MCl₅ [Fig 2(d)] combination showed a similar band at 1633 cm⁻¹, which supports the N-Nb stretching for the PSCPVP-MCl₅ complex. UV spectrum shows Py-MCl₅ (0.25% solutions) exhibits two absorption bands at 250 and 256 nm. Fig. 3(a) shows SEM images of PSCPVP beads. Through FT-IR, the chemical connection between PSCPVP and MCl₅ was discovered. Through elemental analysis, the quantity of each element contained in the PSCPVP-MCl₅ complex catalyst was quantitatively assessed and given in Table 3.

Table 1 — Comparative study for the catalytic efficiency of various Soluble Lewis acid metal complex catalysts for acylation of ethanol with acetic anhydride under pseudo - first order condition, [Ethanol: 17.06 mmol (1 mL); Stirring speed: 400 rpm; Acetic anhydride: 317.4 mmol (30 ml); Temperature: 30°C ± 0.1 and Soluble catalyst: 0.25 mmol].

S. No.	Name of the Catalyst	$k_{\text{obs}} \times 10^3, \text{min}^{-1}$
1	Py- MoCl ₅	11.91
2	Py- TaCl ₅	11.42
3	Py-NbCl ₅	9.63
4	Py- SbCl ₅	2.90

Table 2 — Comparative study for the catalytic efficiency of various Insoluble Lewis acid metal complex catalysts for acylation of ethanol with acetic anhydride under pseudo-first order conditions, [Ethanol: 17.06 mmol (1 ml); Stirring speed: 400 rpm; Acetic anhydride: 317.4 mmol (30 ml); Temperature: 30°C ± 0.1 and Insoluble catalyst: 0.5 mmol].

S. No.	Name of the catalyst	$k_{\text{obs}} \times 10^3, \text{min}^{-1}$
1	PSCPVP- MoCl ₅	7.48
2	PSCPVP- TaCl ₅	6.98
3	PSCPVP-NbCl ₅	6.51
4	PSCPVP- SbCl ₅	1.73



Scheme 4 — Acylation of ethanol with acetic anhydride using PSCPVP-MCl₅

Through SEM examination, the surface morphology of the PSCPVP and PSCPVP-MCl₅ complex catalyst was studied, and the results are presented. The availability of metal and chloride in the Py-MCl₅ and PSCPVP-MCl₅ complex catalyst was also validated using EDAX analysis, as demonstrated in the EDAX analysis of PSCPVP beads there was no characteristic Cl or any other metal peak in Fig. 4(a). The weight loss (decomposition temperature) of chloride was measured using TGA analysis to assess the quantity of chloride contained in the PSCPVP beads and PSCPVP-MCl₅ catalyst. Similarly, the availability of metal and chloride in the PSCPVP-MCl₅ and Py-MCl₅ complex catalyst was also confirmed through EDAX analysis [Fig 4(d) & Fig 5(c)]. The amount of chloride present in the PSCPVP beads and PSCPVP-MCl₅ catalyst was determined from the decomposition temperature (weight loss) of chloride through TGA analysis Fig. 6. Similar to that, Fig. 6(a) shows the

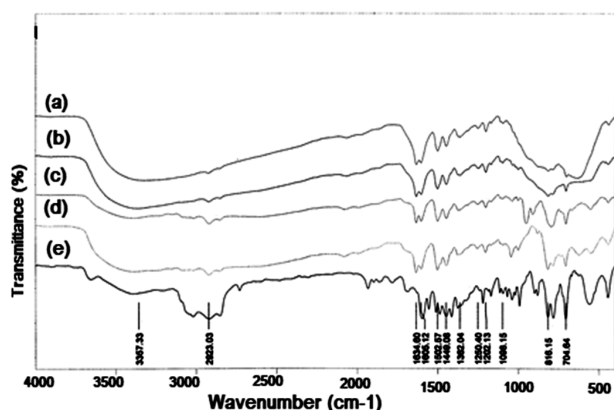


Fig. 1 — Comparative FT-IR spectrum of insoluble catalysts (a) PSCPVP- NbCl₅; (b) PSCPVP-TaCl₅; (c) PSCPVP-MoCl₅; (d) PSCPVP-SbCl₅ and (e) PSCPVP-beads

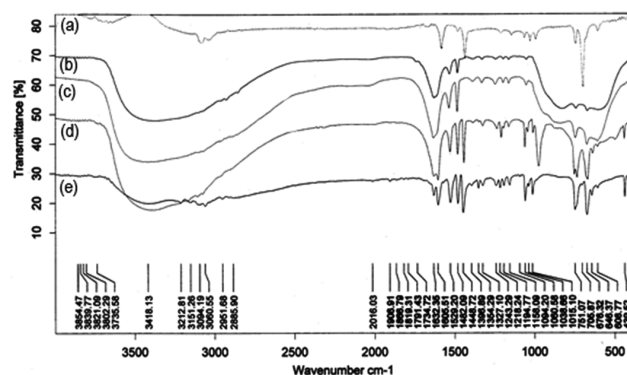


Fig. 2 — Comparative FT-IR spectrum of soluble catalysts (a) Pyridine; (b) Py-NbCl₅; (c) Py-TaCl₅; (d) Py-MoCl₅ and (e) Py-SbCl₅

findings of the TGA investigation of PSCPVP beads Through thermogravimetric analysis [Fig 6(a-e)], it was possible to calculate the breakdown temperature for PSCPVP beads. FT-IR, elemental analysis, SEM, EDAX, and TGA investigations all showed that the PSCPVP beads and MCl₅ formed a complex.

Reusability and recycling of the catalyst

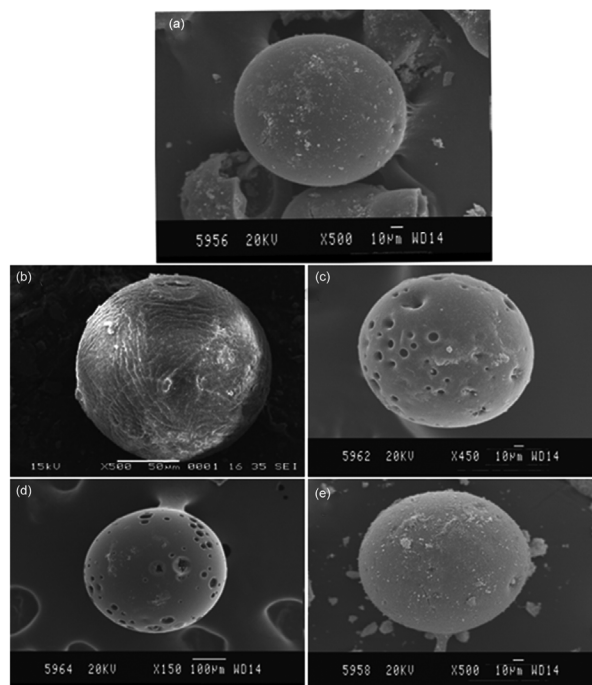
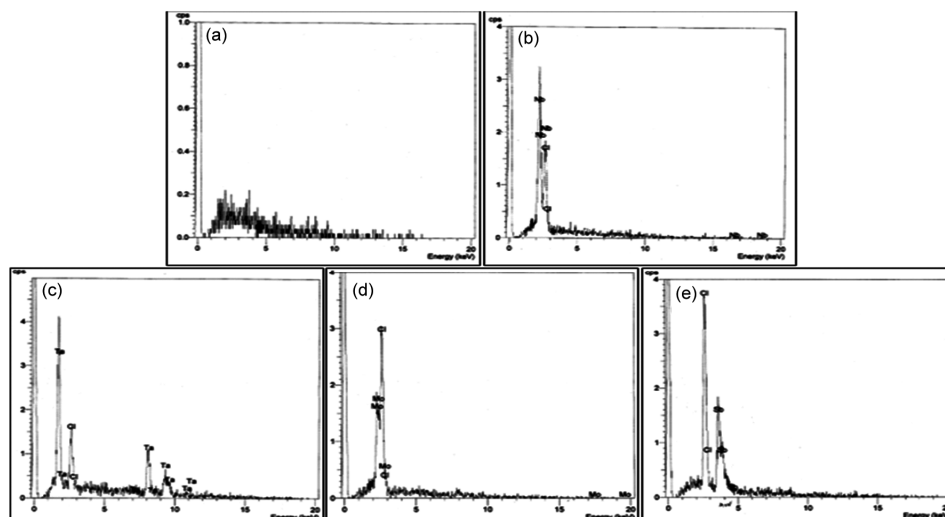
The stability and catalytic activity of polymer-supported Lewis's acid complex catalysts have been examined because, sometimes, the catalytic activity was slightly lowered due to degradation or leaching of metal chlorides. Therefore, the respective polymer-supported metal complex catalysts used in the first cycle have been recovered through filtration and washed with methanol/acetone, and then dried. Then, the irrespective metal complex Lewis's acid catalysts were employed individually to catalyze the acylation of ethanol with acetic anhydride under identical pseudo-first-order conditions as it was maintained in the first cycle. That is, the reusability of insoluble polymer-supported metal complex catalyst PSCPVP-MCl₅ was studied individually by conducting the same acylation of ethanol with acetic anhydride reactions by maintaining the first cycle pseudo-first order experimental conditions. In the acylation reaction, after the completion of the reaction (i.e. first cycle), the polymeric insoluble PSCPVP-MCl₅ catalyst has been easily recovered from the reaction mixture by simple filtration, washed with methanol/acetone 3 times, and then dried at 60°C. Then, the dried catalyst (recovered after the first cycle) was reused to conduct the esterification reaction i.e. second cycle. As usual, the disappearance of ethanol was quantitatively followed through GLC irrespective of catalyst and the pseudo-first-order rate constants were calculated. Again, after the second cycle, the catalyst was recovered and reused for the third cycle and the pseudo-first-order rate constants were calculated by maintaining the same experimental condition. The calculated pseudo-first-order rate constant irrespective of the lewis acid catalyst is given in Table 4.

Comparative study for the efficiency of various insoluble lewis acid metal complex catalysts for acylation reactions

The comparative efficiency study among the 4 types of polymer-supported (insoluble) Lewis's acid complex catalysts reveals that the order of catalytic activity in terms of pseudo-first-order rate constants in acylation reaction is PSCPVP-MoCl₅ > PSCPVP-TaCl₅ > PSCPVP-NbCl₅ > PSCPVP-SbCl₅ (Fig 7).

Table 3 — Comparative relative percentage of C, H, and N elements present in each insoluble polymer-supported Lewis acid complex catalysts

Name of the catalyst	Polymer beads						Metal Chlorides	
	N(%)		C(%)		H(%)		MCl ₅	
	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp
PSCPVP Beads (control)	4.1	3.58	87.9	87.7	7.97	8.09	0.00	0.00
PSCPVP- NbCl ₅	2.2	1.99	49.0	51.3	4.45	5.45	44.1	41.2
PSCPVP- TaCl ₅	2.0	1.56	42.9	40.0	3.89	4.79	51.1	53.6
PSCPVP- MoCl ₅	2.2	2.02	48.8	52.5	4.43	4.99	44.4	40.4
PSCPVP- SbCl ₅	2.1	1.70	46.8	46.8	4.25	4.50	46.6	46.9

Fig. 3 — SEM images of single bead view (a) PSCPVP, (b) PSCPVP-NbCl₅, (c) PSCPVP-TaCl₅, (d) PSCPVP-MoCl₅ and (e) PSCPVP-SbCl₅Fig. 4 — EDAX analysis of (a) PSCPVP Beads, (b) PSCPVP-NbCl₅, (c) PSCPVP-TaCl₅, (d) PSCPVP-MoCl₅ and (e) PSCPVP-SbCl₅

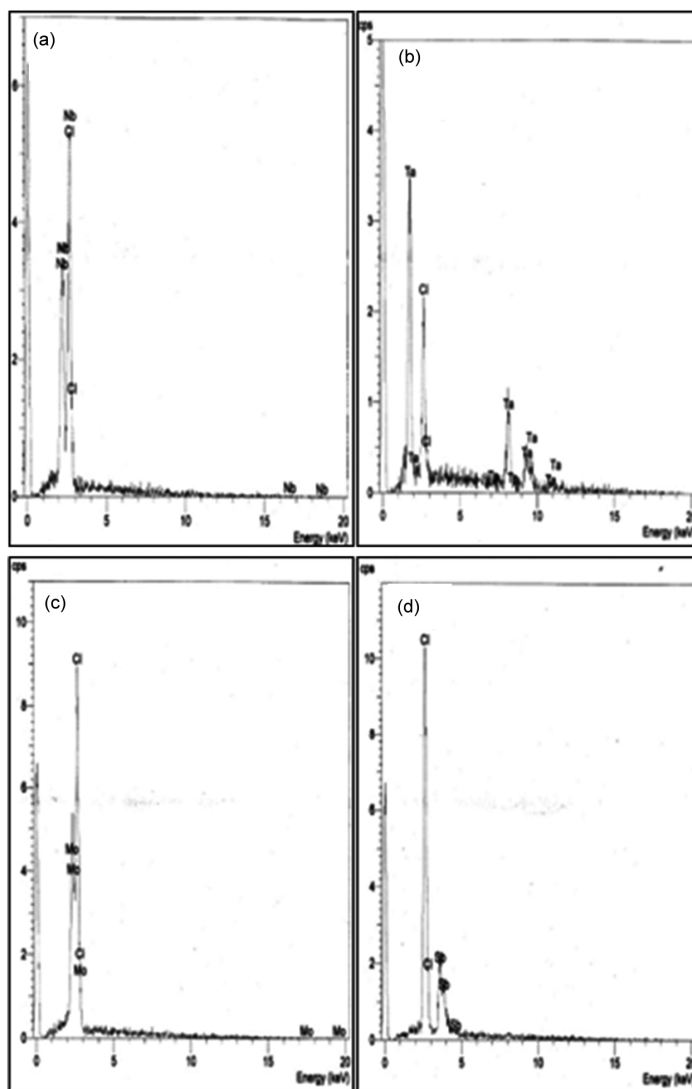


Fig. 5 — EDAX analysis of (a) Py-NbCl₅, (b) Py-TaCl₅, (c) Py-MoCl₅ and (d) Py-SbCl₅

That is, the reactivity trend observed in both reactions is found to be similar to that of soluble Lewis's acid complex catalysts. Therefore, the inferences and their corresponding explanations discussed in the previous section (homogenous catalysis) in connection with the order of reactivity hold good for heterogeneous Lewis's acid catalysts also. However, apart from the Lewis acidity of insoluble complex catalysts, the activity of the catalyst also depends on the nature of the polymeric backbone, degree of hydrophobic attraction between the organophilic polymers with a substrate, porosity of the insoluble microporous beads, swellability of beads concerning crosslinking and size of the organic substrates.

Normally, the soluble form of catalyst always showed higher catalytic activity than their corresponding

insoluble analogs. However, in terms of reusability, the insoluble heterogeneous catalyst was found to attract effectively and thus reduce the pollution and cost of the reaction. Gange *et al.*³⁹ reported a polymer-supported Rhodium catalyst and they proved that it could be reused up to six times with a slight decrease in activity. Above all, the plain Lewis acids such as NbCl₅, TaCl₅, MoCl₅, and SbCl₅ are always unstable due to moisture sensitivity and corrosion. Further, even when these plain Lewis acids are complexed with pyridine ligand, then their storability has improved partially as compared with plain metal chlorides. But, still, the stability of the soluble pyridine-based complex was proved as poor and cannot be used in continuous mode of reactions (or) operation, particularly in the industrial scale preparation.

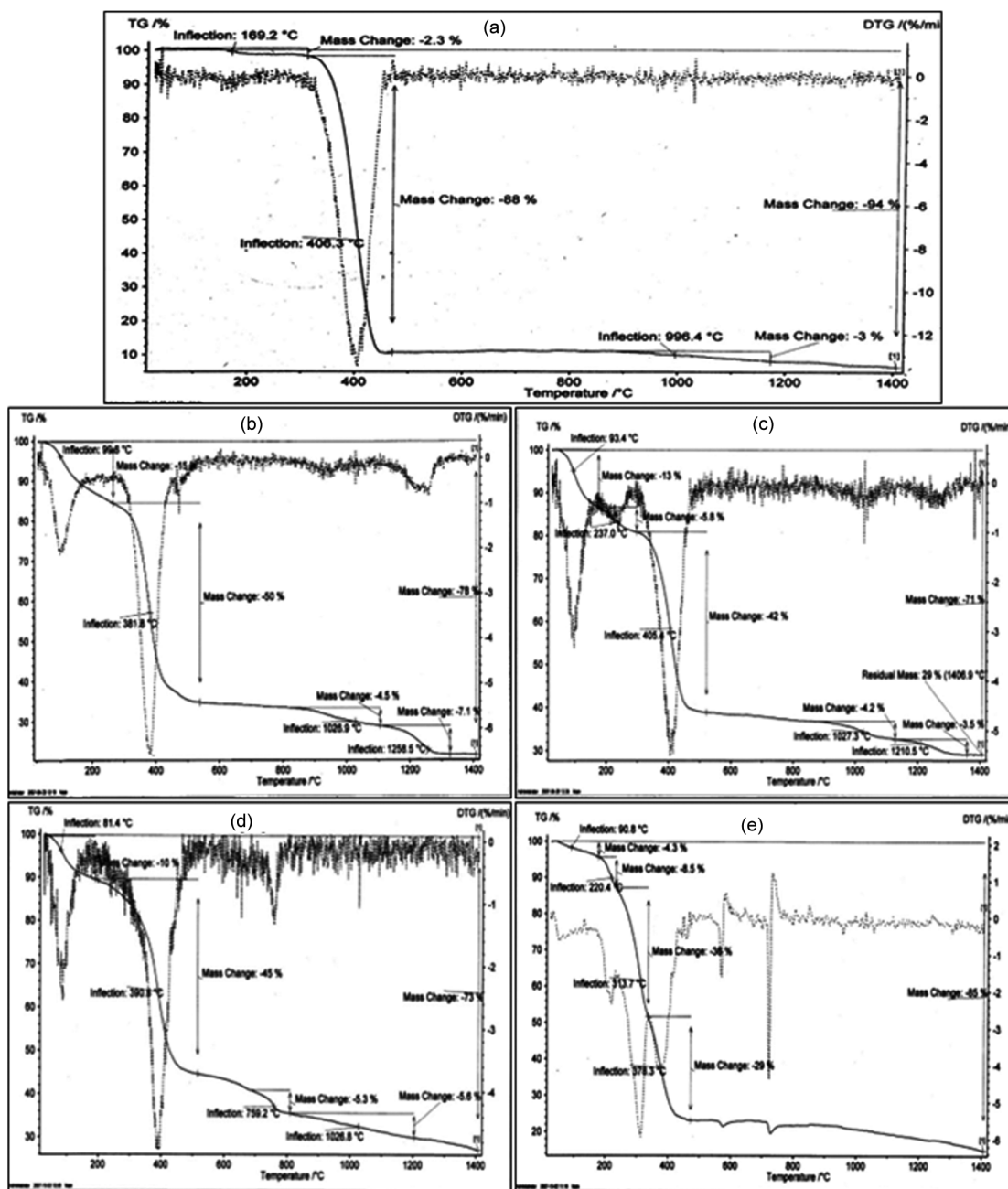


Fig. 6 — TGA analysis of (a) PSCPVP beads, (b) PSCPVP-NbCl₅, (c) PSCPVP-TaCl₅, (d) PSCPVP-MoCl₅ and (e) PSCPVP-SbCl₅

Therefore, it is noteworthy to immobilize the Lewis acid moiety onto the insoluble polymeric backbone containing lone-pair electrons in the nitrogen of 4-vinyl pyridine functionalized with cross-linked poly(styrene) bead-shaped matrix. Belfiore *et al.*⁴⁰ reported the formation of coordination complexes between the nitrogen lone pair on poly(4 vinyl pyridine) and with the metal center in dichloro or tricarbonyl ruthenium(II). More specifically, we have

complexed unstable transition and non-transition metal pentachloride Lewis acids like TaCl₅, NbCl₅, MoCl₅, and SbCl₅ respectively into the bead-shaped cross-linked PSCPVP matrix via the formation of coordination bond with unshared electrons of pyridine and metal chlorides. Therefore, the Lewis acidity of each insoluble complex again depends on the co-ordination number of each metal and the number of interacting ligands (PSCPVP). Added to these factors,

the geometry of the complex and the orientation of the substrate to approach the Lewis acidic site of the complex catalyst also had a role to facilitate the activity. But it is very difficult to establish the order of reactivity based on the geometry of the insoluble PSCPVP-based cross-linked poly(styrene) matrix Lewis's acid complex catalysts as well as the orientation of the substrates. In acylation reaction, the observed trend has exactly similar to the corresponding homogeneous catalysts and hence the reasons described in the soluble catalysts would also substantiate here. And of course, here the various factors of the effect of polymer catalysts as mentioned earlier for esterification reactions have also contributed effectively to facilitating the acylation reaction. Neckers⁴¹ and co-workers had prepared the AlCl_3 coordinated with cross-linked poly(styrene) matrix as a Lewis acid catalyst and proved that the formation of the complex has proceeded via interaction between π electrons of poly(styrene) with AlCl_3 and this insoluble Lewis acid catalyst has effectively facilitated the dithioacetalization of carbonyl compounds and trans-thioacetalization of acetals.

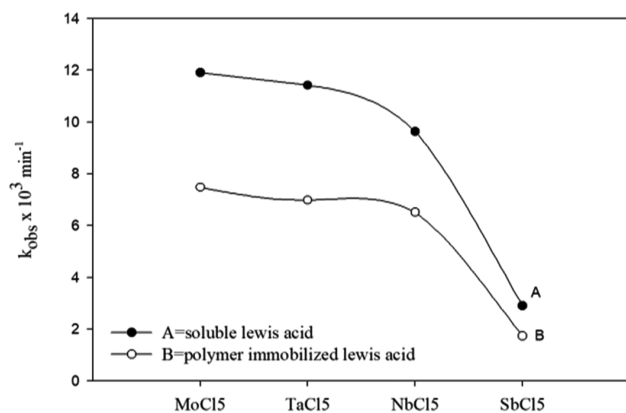


Fig. 7 — Comparative catalytic efficiency for acylation of ethanol using soluble (Plot A) and insoluble (Plot B) Lewis's acid metal chloride complex catalysts

The production of ethyl acetate through the acylation of alcohols normally is an easy process since acetic anhydride possesses two acyl groups. Of the two acyl groups, one group can react with alcohols and produce ethyl acetate and another one leads to the formation of one molecule of acetic acid and this byproduct may also react with remaining alcohol and thus produce an additional amount of ethyl acetate. In other words, we have determined pseudo-first-order rate constant k_{obs} by determining the quantitative disappearance of ethanol against time through GLC analysis, in which, the primary reaction is the reaction of one acyl group with alcohols and the secondary reaction is another acyl group generating acetic acid which in turn react with alcohol. These two types of reactions are responsible for the drastic reduction of ethanol and thus reflected in higher k_{obs} values irrespective of the catalysts when compared with the esterification reaction. Romero *et al.*⁴² reported a similar observation in the synthesis of isoamyl acetate using immobilized lipase-catalyzed acetylation in an n-hexane reaction. Similarly, Sang-gi *et al.*⁴³ also observed the same trend, that is, the reaction between benzyl alcohol with acetic anhydride and benzyl alcohol with acetic acid under identical reaction conditions using metallic Lewis's acid. In which they reveal that the previous one was found to produce a larger amount of benzyl acetate (74 % in 1 h) than with latter one (64 % in 12 h). In other words, the reaction involving acetic anhydride had always given an enhanced amount of acetate than the acid.

Acylation using acetic anhydride M = Nb, Ta, Mo and Sb

The co-ordination complex was used to immobilize less stable Lewis's acids, such as transition metal-based pentachlorides like TaCl_5 , NbCl_5 , and MoCl_5 , as well as non-transition metal pentachloride SbCl_5 , onto the bead-shaped cross-linked PSCPVP matrix. To create a practical and stable Lewis's acid complex, or to improve reusability/increase the number of

Table 4 — Comparative study for the catalytic efficiency of soluble and Insoluble Lewis acid metal complex catalysts for acylation of ethanol with acetic anhydride under pseudo-first order conditions

No of Cycles	Soluble & Insoluble catalyst $k_{\text{obs}} \times 10^3, \text{min}^{-1}$							
	Py-NbCl ₅	PSCPVP-NbCl ₅	Py-TaCl ₅	PSCPVP-TaCl ₅	Py-MoCl ₅	PSCPVP-MoCl ₅	Py-SbCl ₅	PSCPVP-SbCl ₅
1	9.6	6.5	11.4	6.98	11.9	7.48	2.9	1.7
2	-	6.3	-	6.85	-	7.4	-	1.6
3	-	6.30	-	6.79	-	7.32	-	1.5

recycles, improved selectivity, simpler handling, straightforward work-up processes, non-toxicity, non-corrosiveness, and mildness of the reaction conditions, is the primary goal. Above important, the new bead-shaped heterogeneous Lewis acid catalysts are simple to pack in column reactors, allowing for the continuous operation of the esterification and acylation processes and opening the door to larger/industrial scale ester synthesis. The most significant goal of this work has been to find ways to make it simple to recover and reuse materials with regular activity. The stability of the complex has an impact on the catalyst's capacity to be reused. Although the esterification of the acylation process was successfully accelerated by all bead-shaped insoluble heterogeneous Lewis acid complex catalysts in the first cycle, it is necessary and rational to look at the complex's reactivity in the succeeding cycles in order to assess its stability. Because occasionally the added Lewis acid metal chloride MCl_5 may be physically trapped onto the PSCPVP matrix without forming the coordination complex with unshared electrons of 4-vinyl pyridine substituted in PSCPVP, this would easily leach out the metal chlorides (MCl_5) in the first cycle itself and have the potential to reduce catalyst activity. We therefore decided to reuse the catalyst for the esterification of acetic acid with butanol reaction for two additional cycles (excluding the first cycle), regardless of metal chlorides, by adopting the same experimental procedures as they were followed in the respective first cycle catalyst condition. This was done to rule out the possibility of leachability (or) physisorption (or) physical entrapment of MCl_5 onto the PSCPVP matrix. Table 4 lists the observed pseudo-first-order rate constants. The efficiency of PSCPVP- $MoCl_5$ and PSCPVP- $SbCl_5$ are observed to drastically decrease even in the second cycle, it is inferred from the obtained k_{obs} , demonstrating the poor stability of complex (or) leachability of the metal pentachlorides. Particularly, it is discovered that the $SbCl_5$ immobilized compound is inactive even in the third cycle. The fact that $SbCl_5$ underwent reduction and produced a lower state ($Sb V$ to $Sb III$) complex was unquestionably established by this finding. Due to the easy probability of decomposition by the release of chlorine gas, $MoCl_5$ was also shown to have reduced stability (Cl_2). Therefore, it is not appropriate to utilize these two catalysts again. The catalytic activity of the PSCPVP- $TaCl_5$ and PSCPVP- $NbCl_5$ Lewis acid complex

catalysts, in contrast, was found to be maintained even up to the third cycle with barely any reduction from the activity of the first cycle. Therefore, it has been determined that there is no chance of MCl_5 being physically absorbed, trapped, or leached from the PSCPVP matrix. Because MCl_5 may readily leak out of the matrix during the stirring of the reaction, even during the first cycle, if it is physisorbed (or) entrapped onto the matrix. The consistency of activity at the second and third cycles, however, has conclusively shown that $TaCl_5$ and $NbCl_5$ have both formed a stable co-ordination bond with a lone pair of electrons in the pyridine N atom substituted in the PSCPVP matrix, thereby confirming the stability of the corresponding Lewis acid complex.

We have created practical bead-shaped microporous stable PSCPVP- MCl_5 Lewis acid complex catalysts, which in turn actively accelerate the acylation processes, to quickly explain. As a result, these beads may be used to pack the column reactor for continuous mode operation or operation at industrial scale. If activity declines after a few cycles, it is straightforward to regenerate it using the appropriate metal chlorides, such as by swirling MCl_5 with a swollen PSCPVP bead matrix, and it is thus able to restore the original activity. Nissari *et al.*⁴⁴ also studied the reuse of the catalyst in the esterification of tertiary butanol with acetic anhydride using alumina supported $InCl_3$, $GaCl_3$, $FeCl_3$, $CuCl_2$, $NiCl_2$, $CoCl_2$, and $MnCl_2$ moiety and suggested that the activity has maintained even for a third and fourth cycle.

Conclusion

The acylation processes are actively accelerated by the eight distinct types of soluble and practical bead-shaped microporous PSCPVP- MCl_5 ($M = Nb, Ta, Mo$ & Sb) Lewis's acid complex catalysts that have been created. FT-IR, SEM, EDAX, CHN, and TGA tests have been used to characterize each of the eight catalysts. On the basis of determining the pseudo-first-order rate constants, the comparative catalytic efficacy of the soluble and insoluble catalysts has been evaluated. In other words, the rate constants for the acylation of ethanol with acetic anhydride are calculated for the soluble catalysts $Py-NbCl_5$, $Py-TaCl_5$, $Py-MoCl_5$, and $Py-SbCl_5$ as well as the insoluble catalysts PSCPVP- $NbCl_5$, PSCPVP- $TaCl_5$, PSCPVP- $MoCl_5$, and PSCPVP- $SbCl_5$. The stability of the complex and oxophilic attraction have been used to describe the major factors that led to this form of

organization. Similar to this, the four different insoluble catalysts have the following reactivity in the acylation process: PSCPVP-MoCl₅ > PSCPVP-TaCl₅ > PSCPVP-NbCl₅ > PSCPVP-SbCl₅, and the polymeric support and stability of the complex are used to explain why certain catalysts have lower or higher catalytic activity. For the acylation process, it is discovered that the catalytic activity of the soluble Py-NbCl₅, Py-TaCl₅, Py-MoCl₅, and Py-SbCl₅ catalysts was 1.47, 1.63, 1.59, and 1.67-fold more active than PSCPVP-NbCl₅, PSCPVP-TaCl₅, PSCPVP-MoCl₅, and PSCPVP-SbCl₅, respectively. It is feasible to restore the initial activity of insoluble catalysts in the event that it declines after a number of cycles by simply treating them with the appropriate metal chlorides, such as by swirling MCl₅ with swollen PSCPVP beads. For use in continuous mode or on an industrial scale, these beads can be put within a column reactor.

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