Research Article

Hydrophobic Polymer-Supported Lewis Acid for Solid-Phase Synthesis

Sachin Mane, Surendra Ponrathnam and Nayaku Chavan

Polymer Science and Engineering Division National Chemical Laboratory, Pune – 411008, India

*Corresponding author E-mail: nn.chavan@ncl.res.in, Tel: 91-20-25903008

Received: November 5, 2015 Revised: January 20, 2016 Accepted: January 20, 2016 Published: January 21, 2016

Abstract: Conventional unsupported Lewis acids are more sensitive towards moisture rather than substrate resulting into deactivation of the catalyst and difficult to use in an anhydrous reaction. In the present work, deactivation of the conventional Lewis acids was strongly avoided by using hydrophobic polymer-supported Lewis acids (PSLAs). The obtained PSLAs were characterized by different techniques including surface area, particle size, thermostability, glass transition temperature, and morphology. Surface areas of PSLAs were in the range of 50–80 m²/g whereas particle sizes of polymer beads were in the range of 15–35 μm before and after polymer modification. Further, degradation of base polymer and PSLAs were in the range of 440–450°C whereas glass transition temperature (T_g) of base polymer was upto 400°C. However, T_g was attenuated for polymer containing AlCl₃ and further for HgCl₂. Importantly, leakage problem of the Lewis acids was eliminated due to strong co-ordinate bonding between polymer and catalyst.

Keywords: Hydrophobic polymer; Polymer-supported catalyst; Lewis acid; Thermal properties

1. INTRODUCTION

Over the past two decades, much attention has been paid on Lewis acids applications in an organic synthesis, functional group transformation, and activation of the catalyst [1,2]. Lewis acids used in Friedel-Craft alkylation and acylation are well-known. Friedel-Craft reaction using Lewis acid is very old method for the synthesis of C–C bond formation and is still attractive [3]. Polymer-supported Lewis acids (PSLAs) are potentially used in different reactions such as Friedel-Craft alkylation [4,5], acylation [6], hydroxylation [7], and sulfonylation [8,9]. Nowadays, number of methods such as covalent, co-ordinate bonding [10], encapsulation [11], immobilization [12], and embedded [13] is available for anchoring the Lewis acids to polymer support. These methods have their own merits and demerits. Typically, catalysts must have the property of accelerating the reaction by 100 times than non-catalyzed reactions and side reactions must not compete with the desired product formation. Over the last few years, Lewis acids were used at various temperatures depending upon the reaction conditions [14]. For instance, Diels-Alder reaction requires high temperature ranging from 200–600°C [15]. Therefore study of thermal stability of a base polymer and PSLAs are an important prior to use of the beaded polymer in solid-phase synthesis.
In the past, Charles Friedel and James Crafts invented [16] the reaction to attach the substituent to the aromatic ring via electrophilic substitution reaction using unsupported (homogeneous) Lewis acid catalyst. Unsupported Lewis acids have greater affinity towards water or moisture over substrate resulting into deactivation of the catalyst. Due to this reason, unsupported Lewis acids are not only affecting the yield of the reaction but also produces side product. Consequently, hydrophobic, and reactive polymer-supported catalyst was obtained for anhydrous reactions. Due to hydrophobicity of polymer support, catalysts can remain in anhydrated condition for a longer period. Over the last decade, researchers have widely studied the synthesis of polymer and polymer-supported catalysts with desired properties [17,18]. The major problems associated with the polymer-supported Lewis acids is the less catalysts loading which significantly affects the yield of the reaction [19] and leakage of the catalysts during its application. Today, low loading of catalysts, reagent, substrate, and protecting groups is a major concern with solid support. As a consequence, highly reactive primary amine based poly(AA-co-DVB) was synthesized to obtain more loading of catalyst. Mostly, conventional (unsupported) Lewis acids are used in organic reactions which are difficult to separate after completion of reaction. Another problem associated with Lewis acid is that, unsupported Lewis acids can be used only once and discarded after use. To overcome both difficulties, recyclable polymer-supported Lewis acid was obtained which can be easily recovered by filtration and reused for number of cycles [20]. In the present work, hydrophobic and reactive polymer support was obtained to avoid aforementioned concerns. Further, recyclable polymers have potential application in different fields [21].

Limura et al. [22,23] reported the application of hydrophobic polymer-supported catalyst for hydrolysis of thioethers and in formation of C–C bond. In 2014, Sani et al. [24] discussed that, hydrophobic surface of solid support minimizes the deactivation of the catalyst due to water or trace amount of moisture. Most of the organic reactions are carried out in organic solvents such as ethanol, acetone, THF, diethyl ether, and chloroform. As a result, synthesis of polymer with high reactivity and greater hydrophobicity is an essential. To the best of our knowledge, reactive and hydrophobic poly(AA-co-DVB) supported Lewis acids such as AlCl3/HgCl2 have not been reported previously. Furthermore, properties such as surface area, average particle size, thermal analysis, and morphology of PSLAs were also evaluated. Overall, these hydrophobic PSLAs are industrially economical and environmentally benign.

2. EXPERIMENTAL

2.1. Materials

The following chemicals were used as received: Allylamine (99%, Spectrochem), divinylbenzene (85%, Aldrich), cyclohexanol (99%, Loba Chemie, Mumbai), ethanol (99.9%, Changshu Yangyuan Chemical, China), acetonitrile (99%, Spectrochem), 1,4-dioxane (99.9%, Loba Chemie), aluminium(III)chloride (≥98%, Merck), mercury(II)chloride (99.5%, Loba Chemie), 2,2'-azobisisobutyronitrile (99%, SAS Chemicals, Mumbai, India), and poly(vinylpyrrolidone) K90 powder (PVP, mol. wt.: 360,000, Fluka).
2.2. Suspension Polymerization

An aqueous phase (1 wt%) was prepared by dissolving the protective colloid [poly(vinylpyrrolidone)] in deionised water. Then, organic phase was prepared by mixing a monomer (allylamine), crosslinker (divinylbenzene), an initiator (2,2'-azobisisobutyronitrile), and pore generating solvent (cyclohexanol) in a nitrogen atmosphere at room temperature. Synthesis of beaded polymer was conducted in a specially designed polymerization reactor equipped with a constant temperature water bath (thermostat), mechanical stirrer, reflux condenser, and a nitrogen gas inlet. Subsequently, an organic (discontinuous) phase was added to the reactor containing aqueous (continuous) phase under stirring speed at 500 rpm under a nitrogen atmosphere. The reaction temperature was raised to 70°C and stirred for 3 h. Hereinafter, polymer beads were thoroughly washed with water, methanol, finally with acetone, and dried at 60°C under reduced pressure. The polymer beads obtained by suspension polymerization were further purified by a soxhlet extraction [25]. In the present work, different crosslink density (CLD) polymers were obtained. CLD defines the percent moles of crosslinking agent (divinylbenzene) with respect to monomer (allylamine). Feed composition of monomer-crosslinker and reaction conditions of poly(AA-co-DVB) synthesis in suspension polymerization is shown in Table 1.

Table 1. Feed composition of poly (allylamine-co-divinylbenzene) at different CLD

| Polymer code | CLD (%) | Allylamine | Divinylbenzene |
|--------------|---------|------------|----------------|
|              |         | mol        | g              | mol           | g          |
| ADC-5        | 5       | 0.195      | 11.147         | 0.010         | 1.271      |
| ADC-10       | 10      | 0.180      | 10.256         | 0.018         | 2.339      |
| ADC-15       | 15      | 0.166      | 9.496          | 0.025         | 3.248      |
| ADC-20       | 20      | 0.155      | 8.842          | 0.031         | 4.033      |
| ADC-25       | 25      | 0.145      | 8.271          | 0.036         | 4.716      |

Reaction conditions: Batch size – 16 mL; Initiator – 2,2'-azobisisobutyronitrile (2.5 mol%); stirring speed – 500 rpm; reaction time – 3 h; outer phase – H₂O; protective colloid – poly(vinylpyrrolidone); concentration of protective colloid – 1 wt%; porogen – cyclohexanol; porogen concentration – 48 mL (monomer:porogen ratio, 1:3 v/v).
2.3. Preparation of polymer-supported Lewis acid catalyst

Soxhlet purified polymers were used for modification with Lewis acids [26]. Poly(AA-co-DVB) having CLD of 5, 10, 15, 20, and 25% were used for modification with Lewis acids (AlCl₃/HgCl₂). For this, Lewis acid (AlCl₃, 5 g) was dissolved in 50 mL of ethanol and placed at room temperature for 2 days to obtain complete dissolution of Lewis acid. Then, poly(AA-co-DVB) of 5 to 25% CLD (2 g) were taken separately in a glass vial. To this, above Lewis acid solution (10 mL Lewis acid solution in ethanol) was added to each CLD polymer. These polymers were placed at ambient temperature for 2 days to obtain uniform modification of polymers. Subsequently, polymers were washed using ethanol for 3 – 4 times to remove unreacted Lewis acid and polymers were dried at 70°C under reduced pressure. Dried polymers were used for properties evaluation. Aforementioned procedure was also used to modify the polymer with HgCl₂. Poly(AA-co-DVB) synthesized by suspension polymerization using a cyclohexanol was abbreviated as ADC whereas polymer modified using AlCl₃ and HgCl₂ was abbreviated as ADCA and ADCH, respectively. The synthesis of polymer by suspension polymerization and its plausible modification with Lewis acid is represented in Figure 1.

MXn: AlCl₃/HgCl₂

Figure 1. Synthesis of poly(allylamine-co-divinylbenzene) and its plausible modification with Lewis acid

2.4. Characterization

Polymers obtained by a suspension polymerization, purified by soxhlet extraction, and dried at 70°C under reduced pressure were used for characterization. In the present work, base and modified polymers were characterized by different techniques. FT-IR spectra were recorded on Perkin Elmer spectrometer to confirm the polymer synthesis by a model of spectrum GX. The samples were prepared after drying the polymers at 70°C for 8 h. The surface area of polymers was measured using a surface area analyzer NOVA 2000e, Quantachrome. Average particle diameter was determined using an Accusizer 780 (model LE 2500-20) PSS.NICOMP, particle sizing system, Santa Barbara, California, USA. Amine content was determined by acetic anhydride in pyridine using a titrimetric method. Thermal stability (DTG) of polymer was evaluated using a simultaneous thermal analysis (STA, Perkin Elmer), while glass transition temperature was studied using a differential scanning calorimetry Q10 (Thermal analysis). Scanning electron microscopy was used to visualize an external morphology which was performed by Quanta 200-3D, dual beam ESEM microscope wherein thermionic emission tungsten filament was used as an electron source.
3. RESULTS AND DISCUSSION

3.1. Fourier transform infra-red (FT-IR) spectroscopy

FT-IR is widely used technique to confirm polymer synthesis and its modification due to ease of handling, availability and inexpensiveness of the method. In this work, poly(allylamine-co-divinylbenzene) was obtained by suspension polymerization and modified with Lewis acids (AlCl₃/HgCl₂). These syntheses of polymers and its modification were confirmed by scanning the FT-IR spectra using KBr pellet (cm⁻¹). FT-IR spectrum illustrated that, peak at 3367 assigned to primary amine in the polymer matrix. Moreover, peak at 2937, 1727, 1455, and 1250 corresponds to aliphatic –C–H str., ester functionality, methyl C–H asymm. bend., and C–O–C str., respectively. Further, 906 and 797 assigned to aromatic –C–H out-of-plane bending whereas disubstituted ring at para position assigned [27] by 832. Polymer modified Lewis acid revealed the most confirmative peaks for AlCl₃ (1603, 1446), and HgCl₂ (1602, 1445) corresponds to Lewis acids [28] in addition to base polymer peaks. Moreover, FT-IR spectra of base polymer and polymer modified Lewis acid are illustrated in Figure 2.

![FT-IR spectrum of base polymer and PSLAs](image)

**Figure 2.** FT-IR spectrum of base polymer and PSLAs

3.2. Surface area determination

Undoubtedly, polymer efficiency influences by various properties including surface area, reactivity, particle size, shape, and morphology of beaded polymers [29–31]. In the present work, cyclohexanol was used as a porogen to obtain porous polymer. Poly(allylamine-co-divinylbenzene)
obtained by suspension polymerization for 5 and 25% CLD were used for surface area evaluation. Surface area was determined by a nitrogen adsorption-desorption BET method. Results showed that, base polymers have the surface area of 80.78 and 165.41 m$^2$/g for 5 and 25% CLD, respectively. It seems that, surface area was increased with increasing CLD [32,33] because at lower concentration of crosslinker, higher meso and macropores structure formation takes place resulting into lower surface area. In contrast, at higher amount of crosslinker, micro pores formation takes place which leads toward greater surface area. However, polymer-supported AlCl$_3$/HgCl$_2$ demonstrated the surface area of (76.39 and 77.42 m$^2$/g) and (62.28 and 65.35 m$^2$/g) for 5 and 25% CLD, respectively. Further, surface area was attenuated after modification with Lewis acid. Thus, more surface area was obtained for high CLD polymer and attenuated with decreasing CLD [34].

3.3. Amine content determination

Functional group content determination is an accurate and widely used method to determine the polymer reactivity. However, this method allows the determining of functionality which are available for modification and not determine the buried functionality. Hydrophobic, poly(allylamine-co-divinylbenzene) was synthesized by suspension polymerization from 5 to 25% CLD and polymer reactivity was evaluated by amine content determination using well-known acetic anhydride in pyridine method, titrimetrically [35]. It was observed that, theoretical amine content was 15.7, 14.3, 13.0, 12.0, and 11.2 mmol/g whereas observed amine content was 4.0, 3.1, 2.7, 2.2, and 1.9 mmol/g for 5, 10, 15, 20, and 25% CLD, respectively. Results clearly revealed that, amine content was decreased with increasing CLD since allylamine concentration was decreased with increasing CLD in polymer composition. Further, observed amine content is much lower compared to theoretical amine content. This is mainly due to amine functionality is well-buried into the polymer matrix consequently not available for titrimetric determination.

3.4. Particle size determination

Particle is also one of the important parameter which affects polymer efficiency. In reality, number of factors such as polymerization method, stirring speed, and type of porogens (solvating/non-solvating) are the major factors which attributes to the particle size of synthesized polymer. Indeed, suspension polymerization is able to provide the particle size in the range of 10–200 µm. In the present work, poly(allylamine-co-divinylbenzene) beads having 5 to 25% CLD were obtained by suspension polymerization using a cyclohexanol porogen. The particle size of the base polymer was 32.07 and 17.36 µm for 5 and 25% CLD, respectively. However, particle size was slightly increased for polymer modified AlCl$_3$ (34.15 and 18.11 µm) and HgCl$_2$ (32.47 and 20.10 µm) for 5 and 25% CLD, respectively. Results demonstrated that, particle size was slightly attenuated with increasing CLD [36] due to highly crosslinked polymers may have the compact binding between monomer and crosslinker. Further, polymer modified Lewis acid showed the slightly higher particle size compared to base polymer perhaps due to surface modification with Lewis acid. Polymer beads obtained by suspension polymerization have the particle size in the range 15–35 µm. The average particle sizes of base and PSLAs are illustrated in Figure 3.
3.5. Differential thermogravimetric analysis

Nowadays, Lewis acids have potentially used in different organic reactions (alkylation, acylation, and so on) [37,38]. In the past, Lewis acids were not only used at room temperature but in high temperature reactions also. As a result, study of degradation temperature of poly(AA-co-DVB) is an essential. Differential thermogravimetric analysis was carried out in a nitrogen overlay by a simultaneous thermal analysis (STA, Perkin Elmer). Results clearly revealed that, degradation temperature ($T_{\text{max}}$) of ADC (446 and 435°C), ADCA (448 and 435°C), and ADCH (448 and 444°C) for 5 and 25% CLD, respectively. It is noteworthy that, $T_{\text{max}}$ of both (unmodified and modified) polymers are in the range of 430–450°C. There is no big difference in the $T_{\text{max}}$ of polymer with respect to CLD due to small change in CLD. Degradation temperature ($T_{\text{max}}$) of base as well as PSLAs is represented in Figure 4.

3.6. Differential scanning calorimetry

Differential scanning calorimetry (DSC) is also one of most important thermal property which demonstrated the polymer safe temperature for application perspectives. Recently, Lewis acids are widely used in many thermal reactions [39,40] consequently, polymer glass transition temperature ($T_g$) evaluation is crucial before applications of polymer as a support [41]. DSC of unmodified and modified polymers was carried out in a nitrogen overlay by DSC, Q-10 (Thermal Analysis). Results clearly showed the $T_g$ of ADC (414 and 405°C), ADCA (256 and 249°C), and ADCH (285 and 275°C) for 5 and 25% CLD, respectively. This study illustrated that, glass transition temperature ($T_g$) of base polymer was slightly decreased with increasing CLD. Moreover, $T_g$ of polymer support was decreased after modification of Lewis acid. Thus, $T_g$ attenuation is more for polymer-supported AlCl$_3$ followed by HgCl$_2$.
Obviously, use of polymer below glass transition (T_g) temperature attributes for better polymer efficiency. Polymer used at or above T_g can make interaction with reactant or reaction medium and interfere with product purity. As a result, the use of polymer below T_g offers an extra pure product in solid-phase synthesis. DSC curves of base and PSLAs are represented in Figure 5.

Figure 4. DTG thermograms of base polymer and PSLAs

Figure 5. DSC thermograms of base polymer and PSLAs
Figure 6. SEM images of base ADC (a,b) and PSLAs, ADCA (c,d), ADCH (e,f) for 5 and 25% CLD, respectively (2500X magnification)
3.7. Surface morphology

Scanning electron microscopy (SEM) is a powerful tool to observe surface morphology and porosity of polymer microbeads. Porous polymer could be used in organic synthesis, functional group transformation, and biomedical fields [42,43]. SEM images of base polymer and PSLAs were scanned for 5 and 25% CLD. The polymer beads were mounted on copper grid and placed below electron beam to observe the surface morphology of beaded microsphere. Rigid morphological structures of polymers were observed before and after modification with catalyst. Interestingly, difference in surface morphology of base and PSLAs were observed which revealed the successful modification of polymer. Base polymers and PSLAs were demonstrated the porous properties [44,45] which significantly improves the efficiency of PSLAs. This porosity of polymer is mainly due to the use of non-solvating porogen during polymer synthesis. SEM images of base and PSLAs at 2500X magnification is represented in Figure 6.

3.8. Energy dispersive X-ray analysis

Energy dispersive X-ray (EDX) spectroscopy is a well-known tool to evaluate the qualitative and quantitative elemental composition in polymer matrix. In the present study, EDX analysis of base polymer and PSLAs were evaluated by a Quanta 200-3D, dual beam ESEM microscope with thermionic emission tungsten filament as an electron source. The base polymer showed that, polymer contains carbon and nitrogen only whereas PSLAs demonstrated the presence of aluminium and mercury in their respective polymers along with carbon and nitrogen. It was observed that, loading of aluminium and mercury was 5.2 and 2.9 at% for 5% CLD polymer which were significantly attenuated to 3 and 1 at% for 25% CLD of polymer, respectively. Hydrogen in the polymer matrix is not detected due to instrument

Figure 7. EDX analysis (at%) of PSLAs
limitation. Result demonstrated the higher concentration of aluminium and mercury metal for 5% CLD which was attenuated for higher CLD polymer. Polymer modification is greater for lower crosslink polymer mainly because of more reactivity of polymer at low CLD. EDX analysis (at%) of base and PSLAs at different CLD is represented in Figure 7.

4. CONCLUSIONS

Hydrophobic polymer-supported Lewis acid was obtained as a heterogeneous catalyst for anhydrous reactions. High Lewis acid loading was observed due to reactive amine based polymer. Moreover, Lewis acid leakage problem was possibly solved since highly reactive primary amine functionality strongly binds Lewis acid; consequently, polymer promises for more turn over number. Trace amount of moisture can deactivate the Lewis acid which was avoided by incorporating hydrophobic crosslinker into the beaded polymer. Average particle sizes of base and polymer modified Lewis acid were in the range of 15–35 μm. Moreover, differential thermal analysis of polymer modified Lewis acid demonstrated that, degradation temperature is in the range of 440–450°C. Differential scanning calorimetry showed that, base polymer has safe temperature at or below 400°C whereas safe temperature was attenuated to 240°C or below for PSLAs. Acid content illustrated the polymer reactivity. Low CLD polymer has more reactivity than higher crosslink polymer. Notably, high Lewis acid loading was observed with low crosslinked polymer compared to high crosslinked polymer. Obviously, a polymer obtained in the present work not only promises to support the Lewis acid but could be used as a support for various catalyst, reagent, substrate, or scavenger.

ACKNOWLEDGMENT

This research was financially supported by University Grant Commission (UGC), New Delhi, India. The authors express their gratitude toward UGC for the award of research fellowship [Fellowship Award No.: Sr. No.: 2061010407; Ref. No.: 20-06/2010(i)EU-IV].

REFERENCES

[1] Roberts, C. C.; Matiás, D. M.; Goldfogel, M. J.; Meek, S. J. Lewis acid activation of carbodicarbene catalysts for Rh-catalyzed hydroarylation of dienes. J. Am. Chem. Soc. 2015, 137, 6488–6491.

[2] Stein, T.; Perez, M.; Dobrovetsky, R.; Winkelhaus, D.; Caputo, C. B.; Stephan, D. W. Electrophilic fluorophosphonium cations in frustrated Lewis pair hydrogen activation and catalytic hydrogenation of olefins. Angew. Chem. Int. Ed. 2015, 54, 10178–10182.

[3] Yamashita, Y.; Saito, Y.; Imaizumi, T.; Kobayashi, S. A Lewis acid/metal amide hybrid as an efficient catalyst for carbon–carbon bond formation. Chem. Sci. 2014, 5, 3958–3962.

[4] Smith, A. G.; Johnson, J. S. Lewis acid-promoted Friedel–Crafts alkylation reactions with α-ketophosphate electrophiles. Org. Lett. 2010, 12(8), 1784–1787.
[5] Ahn, S.; Song, Y. S.; Yoo, B. R.; Jung, I. N. Lewis acid-catalyzed Friedel–Crafts alkylation of Ferrocene with Allylchlorosilanes. *Organometallics* **2000**, *19*, 2777–2780.

[6] Ghodke, S. V.; Chudasama, U. V. Friedel-Crafts alkylation and acylation of aromatic compounds under solvent free conditions using solid acid catalysts. *Int. J. Chem. Stud.* **2015**, *2*(5), 27–34.

[7] Ishimaru, T.; Shibata, N.; Nagai, J.; Nakamura, S.; Toru, T.; Kanemasa, S. Lewis acid-catalyzed enantioselective hydroxylation reactions of oxindoles and β-keto esters using DBFOX ligand. *J. Am. Chem. Soc.* **2006**, *128*, 16488–16489.

[8] Lee, D.; Williamson, C. L.; Chan, L.; Taylor, M. S. Regioselective, borinic acid-catalyzed monoacylation, sulfonylation and alkylation of diols and carbohydrates: Expansion of substrate scope and mechanistic studies. *J. Am. Chem. Soc.* **2012**, *134*, 8260–8267.

[9] Borujeni, K. P.; Tamami, B. Friedel-Crafts acylation of arenes with carboxylic acids using silica gel supported AlCl₃. *Catal. Commun.* 2007, *8*(8), 1191–1196.

[10] Qin, Y.; Jakle, F. Formation of polymeric Lewis acid–Lewis base complexes with well-defined organoboron polymers. *J. Inorg. Organomet. Polym. Mater.* **2007**, *17*, 149–157.

[11] Sirattnai, K.; Damronglerd, S.; Omi S.; Roengsumran, S.; Petsomc, A.; Ma, G. H. Encapsulated AlCl₃: a convenient catalyst for the alkylation of benzene with dodecene. *Tetrahedron Lett.* **2002**, *43*, 4555–4557.

[12] Chiang, C. T. Lewis acid catalysts supported on porous polymer substrate. Patent No. US 05,770,539, 1998.

[13] Sundararaman, A.; Victor, M.; Varughese, R.; Jakle, F. A family of main-chain polymeric Lewis acids: Synthesis and fluorescent sensing properties of boron-modified polythiophenes. *J. Am. Chem. Soc.* **2005**, *127*, 13748–13749.

[14] Spitler, E. L.; Dichtel, W. R. Lewis acid-catalysed formation of two-dimensional phthalocyanine covalent organic framework. *Nature Chem.* **2010**, *2*, 672–677.

[15] Parangi, T. F.; Patel, R. M.; Chudasama, U. V. Acid induced mesoporous S-MCM-41 as solid acid catalyst for friedel-crafts alkylation and acylation. *J. Curr. Chem. Pharm. Sci.* **2014**, *4*(2), 91–109.

[16] Friedel, C.; Craft, J. M. Sur une nouvelle méthode générale de synthèse d’hydrocarbures, d'acétones, etc. *Compt. Rend.* **1877**, *84*, 1392 and 1450.

[17] Ma, H.; Bao, Z.; Bai, L.; Cao, W. A new facile route to chlorination of alcohols via lewis acid AlCl₃. *J. Org. Chem.* **2012**, *2*, 21–25.

[18] Ruicheng, R. A. N.; Diankui, F. U. Polymer supported Lewis acid catalysts. Polystyrene bonded stannic chloride catalyst. *Chin. J. Polym. Sci.* **1991**, *9*, 79–85.
[19] Adams, R.; Adams, E. W. Pinacol hydrate. *Org. Synth.* 1925, 5, 87–89.

[20] Rahmatpour, A. Polystyrene-Supported AlCl₃ as a Highly active and reusable heterogeneous Lewis acid catalyst for the one-pot synthesis of quinoxalines. *Heteroat. Chem.* 2012, 23(5), 472–477.

[21] Mane, S.; Ponrathnam, S.; Chavan, N. Selective solid-phase extraction of metal for water decontamination. *J. Appl. Polym. Sci.*, 2015, 133. DOI: 10.1002/app.42849.

[22] Iimura, S.; Manabe, K.; Kobayashi, S. Hydrophobic polymer-supported catalyst for organic reactions in water: acid-catalyzed hydrolysis of thioesters and transprotection of thiols. *Org. Lett.* 2003, 5(2), 101–103.

[23] Iimura, S.; Manabe, K.; Kobayashi, S. Hydrophobic polymer-supported scandium catalyst for carbon–carbon bond-forming reactions in water. *Tetrahedron*, 2004, 60(35), 7673–7678.

[24] Sani, Y. M.; Daud, W. H. A. W.; Aziz, A. R. A. Activity of solid acid catalysts for biodiesel production: A critical review. *Appl. Catal. A* 2014, 470, 140–161.

[25] Luque de Castro, M. D.; Garcia-Ayuso, L. E. Soxhlet extraction of solid materials: an outdated technique with a promising innovative future. *Anal. Chim. Acta* 1998, 369, 1–10.

[26] Kobayashi, S Jpn. Sci. Technol. Corp. Microencapsulate Lewis acid, EP1069127 A1, 2001.

[27] Bartholin, M. Styrene-divinylbenzene copolymers, revisited IR analysis. *Macromol. Chem. Phys.* 1981, 182, 2075–2085.

[28] Djomgoue, P.; Njopwouo, D. FT-IR spectroscopy applied for surface clays characterization. *J. Surf. Eng. Mater. Adv. Technol.* 2013, 3, 275–282.

[29] Hwang, M. L.; Lee, Y. S.; Kim, T. G.; Yang, G. S.; Park, T. S.; Lee, Y. S. Synthesis of hydroxylated macroporous polymer beads for microwave-assisted desorption of nonpolar volatile organic compounds. *Bull. Korean Chem. Soc.* 2010, 31, 2395–2398.

[30] Mane, S.; Ponrathnam, S.; Chavan, N. Role of interfacial tension of solvating diluents and hydrophilic–hydrophobic cross-Linkers in hyper-cross-linked solid supports. *Ind. Eng. Chem. Res.*, 2015, 54, 6893–6901.

[31] Mane, S.; Ponrathnam, S.; Chavan, N. Design and synthesis of cauliflower-shaped hydroxyl functionalized core-shell polymer. *Des. Monomers Polym.*, 2015, 18, 723–733.

[32] Pujari, N. S.; Vishwakarma, A. S.; Pathak, T. S.; Kotha, A. M.; Ponrathnam, S. Functionalized polymer networks: synthesis of microporous polymers by frontal polymerization. *Bull. Mater. Sci.* 2004, 27, 529–535.
[33] Mane, S.; Ponrathnam, S.; Chavan, N. Synthesis and characterization of hypercrosslinked hydroxyl functionalized co-polymer beads. *Eur. Polym. J.* **2014**, *59*, 46–58.

[34] Okay, O. Macroporous copolymer networks. *Prog. Polym. Sci.* **2000**, *25*, 711–779.

[35] Vogel, A. I. Elementary practical organic chemistry, part-III, quantitative organic analysis, (Lond.), Chapter XIX **1958**, *2*, 697.

[36] Banerjee, S.; Chaurasia, G.; Pal, D.; Ghosh, A. K.; Ghosh, A.; Kaity, S. Investigation of crosslinking density for development of novel penetrating polymer network (IPN) based formulation. *J. Sci. Ind. Res.* **2010**, *69*, 777–784.

[37] Ahn, S.; Song, Y. S.; Yoo, B. R.; Jung, I. N. Lewis Acid-Catalyzed Friedel–Crafts alkylation of Ferrocene with Allylchlorosilanes. *Organometallics* **2000**, *19*, 2777–2780.

[38] Kawamura, M.; Cui, D. M.; Hayashi, T.; Shimada, S. Lewis acid-catalyzed Friedel–Crafts acylation reaction using carboxylic acids as acylating agents. *Tetrahedron Lett.* **2003**, *44*, 7715–7717.

[39] Bei, Y.; Liu, Q.; Feng, S. Effects of Lewis acids on the thermal rearrangements of chloromethylsilane: A density functional theory study. *Silicon* **2013**, *5*, 263–269.

[40] Behbahani, F. K.; Sasani, M. Facile synthesis of bis(indolyl)methanes using iron(III) phosphate. *J. Serb. Chem. Soc.* **2012**, *77*, 1157–1163.

[41] Zhang, B.; Ma, Y.; Chen, D.; Xu, J.; Yang, W. Preparation of poly(styrene-co-isobornyl methacrylate) beads having controlled glass transition temperature by suspension polymerization. *J. Appl. Polym. Sci.* **2013**, *129*, 113–120.

[42] Mane, S.; Ponrathnam, S.; Chavan, N. Interfacial tension approach toward drug loading with two-dimensional crosslinked polymer embedded gold: Adsorption kinetics evaluation. *Int. J. Polym. Mater. Polym. Biomater.*, **2015**, *65*(4), 168–175.

[43] Mane, S.; Ponrathnam, S.; Chavan, N. Hyperhydrophilic three-dimensional crosslinked beads as an effective drug carrier in acidic medium: adsorption isotherm and kinetics appraisal. *New J. Chem.*, **2015**, *39*, 3835–3844.

[44] Hong, L. S.; Lai, J. H. T. Pore structure modification of porous support by PPCVD: A technique to reduce permeability loss. *J. Chin. Inst. Chem. Eng.* **1999**, *30*, 189–197.
[45] Wei, X.; Wang, Z. J.; Wang, S. *Membr. Water Treat.* **2012**, *3*, 35.

*The authors declare no conflict of interest*

© 2016 By the Authors; Licensee Borderless Science Publishing, Canada. This is an open access article distributed under the terms and conditions of the Creative Commons Attribution license http://creativecommons.org/licenses/by/3.0