



Preparation, structure, and catalytic activity of aluminum chloride immobilized on cross-linked polyvinyl alcohol microspheres

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ABSTRACT

Aluminum chloride was covalently bound to cross-linked polyvinyl alcohol (CPVA) microspheres, giving rise to polymer-supported Lewis acid catalysts CPVA- AlCl_3 with a high loading (2.07 mmol/g). Their chemical structures were characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, atomic absorption spectrometry, and chemical analysis methods. The catalytic activity of CPVA- AlCl_3 as well as the relationship between structure and activity was investigated by using Friedel–Crafts acylation reaction of polystyrene. These results suggest that during the immobilization process the structure of the bound aluminum chloride gradually changed from the monomeric form ($-\text{AlCl}_2$) to the dimeric form ($-\text{Al}_2\text{Cl}_5$). The presence of $-\text{Al}_2\text{Cl}_5$ gives rise to a catalytic activity enhancement, and the activities of various forms of CPVA- AlCl_3 follow an order: CPVA- Al_2Cl_5 > transitional form > CPVA- AlCl_2 . In addition, this kind of immobilized Lewis acid catalyst has excellent recyclability and reusability, and in particular, CPVA- Al_2Cl_5 displayed an extremely low extent of catalyst deactivation in the repeated acylation reactions.

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1. Introduction

Lewis acid catalysts find widespread application in the chemical industry as the classic catalysts for Friedel–Crafts acylation and alkylation reactions. They can also be used in polymerization and isomerization reactions of hydrocarbons due to outstanding catalytic activity [1]. Nevertheless, several defects, such as intractability of separation from products, difficulty of recovery and recycling, generation of acidic wastewater during post treatment, high deliquescence, and low product selectivity, exist in the free Lewis acid catalysts and limit their industrial applications. In contrast, immobilized Lewis acid catalysts prepared by immobilizing Lewis acids on solid supports such as inorganic materials or polymeric microspheres can remedy these defects and maximize their value for industrial catalysis [2–5], namely, it is a preferable route for the Friedel–Crafts acylation and alkylation reaction systems in the organic synthesis to use the heterogeneous Lewis acid catalysts. To substitute the heterogeneous Lewis acid catalysts for the homogeneous Lewis acid catalysts is significant for moving the chemical industry toward a more environmentally friendly and economical future.

In the past few decades, great efforts have been devoted to the preparation of immobilized Lewis acid catalysts. Researchers employed silica [6–11], zeolite [12–16], graphite [17,18], montmorillonite [19], polystyrene [20,21], etc. as supports to immobilize Lewis acids via microporous physisorption or chemical bonding methods. During catalytic reactions, however, immobilized Lewis acid catalysts prepared via physisorption were prone to desorb Lewis acids from their supports [22], so that the catalysts obtained via Lewis acid–base coordination or covalent bonding have attracted much attention in recent years [23–28]. Scientists have been researching in this area continuously. However, those immobilized Lewis acid catalysts are rarely applied in practical industrial production due to various reasons such as cost, life, preparation, usage, patent, activity, selectivity, toxicity, physical property, and so on. As a result, novel supports and manifold immobilized Lewis acid catalysts need to be developed vigorously to facilitate their widespread application in industrial catalysis.

In the present study, we prepared an immobilized Lewis acid catalyst CPVA- AlCl_3 , for which cross-linked polyvinyl alcohol (CPVA) microspheres were used as support, and AlCl_3 was immobilized onto CPVA microspheres via covalent bonding. Furthermore, in order to fully estimate the catalytic activity of the immobilized Lewis acid catalyst CPVA- AlCl_3 , it was used in the Friedel–Crafts acylation reaction of polystyrene that was dissolved in a solvent (CCl_4). The advantage of this practice is that after ending the reaction, the acylated product (chloroacylated polystyrene) was easy to be separated by adding precipitator, and it was beneficial for the

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determination of acylation degree of the product. Compared with analogues reported in the literature [27–33], Lewis acid loading on CPVA- AlCl_3 is the most. We found that the high loading results from considerable bonding sites on CPVA microspheres and dimerization of immobilized aluminum chloride. During the immobilization process, the structure of bound aluminum chloride on CPVA microspheres gradually changes from the monomeric form ($-\text{AlCl}_2$) to the dimeric form ($-\text{Al}_2\text{Cl}_5$). More importantly, the dimeric Lewis acid catalyst, i.e. CPVA- Al_2Cl_5 , has a much stronger catalytic activity than CPVA- AlCl_2 . The high loading and dimeric form of aluminum chloride afford CPVA- AlCl_3 excellent catalytic properties including high activity and fine recycling performance. It can be expected that CPVA- AlCl_3 will be promising and potential in the future industrial catalysis.

2. Experimental

2.1. Materials and instruments

Polyvinyl alcohol (PVA, a polymerization degree of 2200), sorbitan monostearate, and liquid paraffin were obtained from Tianjin University Chemical Reagent Plant. Glutaraldehyde (aqueous solution of 50 wt.%) was purchased from Baishi Chemical Engineering Company. Aluminum chloride was supplied by Fuchen Chemical Reagent Plant. Polystyrene ($M_r = 4.7 \times 10^4$) was purchased from Yanshan Petrochemical Company. Other chemicals were obtained from Tianjin Damao Chemical Reagent Plant. The instruments used in this work were scanning electron microscope (SEM, LEO, 438VP), Fourier transform infrared spectrometer (Lambda, FTIR-7600), atomic absorption spectrometer (Unicam, Solaar M6), and oxygen bomb calorimeter (Parr, 6300).

2.2. Synthesis and characterization of support CPVA

CPVA microspheres were prepared by a direct cross-linking method in a suspension system. Dispersant sorbitan monostearate (1.28 g) was dissolved in 160 ml of liquid paraffin forming continuous phase (oil phase), and the oil phase was added into a round-bottom flask fitted with a mechanical agitator, a reflux condenser, and a thermometer. PVA aqueous solution (64 ml) with a concentration of 5 wt.% and 8 ml of glutaraldehyde were mixed to constitute dispersed phase (water phase), followed by adding 10 ml of hydrochloric acid (1 mol/L) as catalyst. The water phase was transferred into the oil phase, and the mixture was fully stirred to make the system thoroughly dispersed, forming a reversed phase suspension system. The system was then heated up to 65 °C, and the cross-linking reaction was conducted with stirring for 6.5 h. After that, the resultant microspheres were thoroughly washed with diethyl ether and distilled water, and were dried under vacuum to constant weight, producing semitransparent CPVA microspheres.

The infrared spectrum of CPVA microspheres was determined by the KBr pellet method to characterize their polyhydroxy cross-link structure. Their morphology was observed with SEM, and the mean grain size was determined with a biological microscope equipped with a micrometer.

2.3. Preparation and characterization of catalyst CPVA- AlCl_3

The preparation experiments were conducted under argon atmosphere and anhydrous conditions. In a flask fitted with a mechanical stirrer, a gas inlet, a thermometer, and a reflux condenser connected with a trap for absorbing the hydrogen chloride evolved, 1 g of CPVA microspheres and 20 ml of chloroform were placed. The microspheres were swollen overnight. Argon gas was bubbled through the content in the flask for 30 min to remove air, in which water vapor was contained. Aluminum chloride powder

(0.5 g) was dissolved in 80 ml of chloroform, and then the solution was poured into the flask. The immobilization reaction was performed with stirring at 40 °C under argon atmosphere. After finishing the reaction, in order to remove the adsorbed substances, the resultant microspheres were washed with chloroform repeatedly until no aluminum chloride was detected in the cleaning liquid (tested by dropping AgNO_3 solution). Finally, the microspheres were dried under vacuum to constant weight and then were stored in a desiccator. The immobilization reactions were performed in different periods of time, giving different samples of CPVA- AlCl_3 , whose chemical structures were diverse and would be characterized as follows.

For the samples obtained in different reaction periods, their loadings of aluminum and chlorine elements were determined. The chlorine content was evaluated by chemical analysis methods. The accurately weighed sample of CPVA- AlCl_3 microspheres was placed in an Erlenmeyer flask, and HNO_3 solution of a given amount was then added. The reaction between HNO_3 and immobilized AlCl_3 was carried out for 3 h at room temperature. After that, the microspheres were isolated by filtration and washed thoroughly with distilled water. The cleaning liquid was incorporated with the filtrate, and its chlorine content was determined by the Volhard method to estimate the loading of the chlorine element on CPVA- AlCl_3 microspheres. In addition, quantitative aluminum analysis was made by atomic absorption spectrometry, and the loading of aluminum element was then calculated. The infrared spectrum of CPVA- AlCl_3 was determined by the KBr pellet method, and by comparison with that of CPVA, the chemical structure of CPVA- AlCl_3 was ascertained.

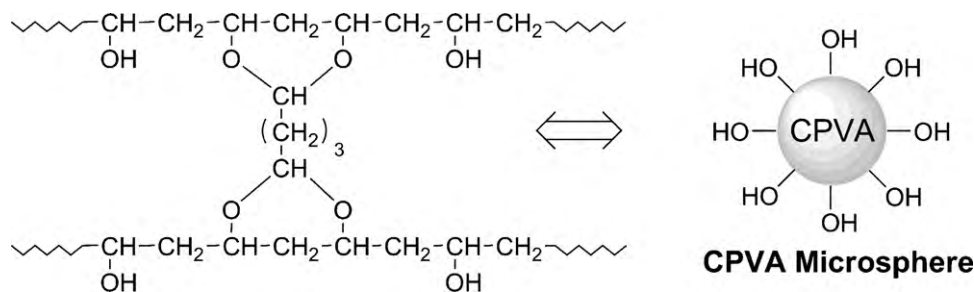
2.4. Testing of catalyst CPVA- AlCl_3

Catalytic activity measurements were carried out for Friedel–Crafts acylation reaction of polystyrene. Chloroform solution (40 ml), in which 5 wt.% of polystyrene was dissolved, and chloroacetyl chloride (1.6 ml) were added into a flask equipped with a mechanical stirrer and a reflux condenser, followed by adding a given amount of CPVA- AlCl_3 microspheres, in which 10.35 mmol of aluminum loading was contained (it needs to be pointed out that for CPVA- AlCl_3 microspheres with different forms, the added amounts of the microspheres were different, but that the added amount of aluminum loading was fixed at 10.35 mmol). The Friedel–Crafts acylation reaction (it is actually a chloroacylation reaction of polystyrene) was performed at room temperature for 5 h. The catalysts were then filtered out and washed with chloroform for recycling, and the cleaning liquid was collected and incorporated with the filtrate. Chloroacylated polystyrene (CAPS) in the filtrate was precipitated with ethanol. The resultant precipitate was thoroughly washed with distilled water and ethanol, and was dried under vacuum. An accurately weighed sample of CAPS was first burned out in an oxygen bomb, and the chlorine element in the sample was fully transformed into chloride ions. Subsequently, the Volhard method was adopted to analyze the chlorine content (wt.%), and the conversion of polystyrene repeating unit was further calculated [34]. In order to examine the recyclability and reusability of CPVA- AlCl_3 , those recovered and treated catalysts were repeatedly used in the chloroacylation reactions of polystyrene under the same reaction conditions.

3. Results and discussion

3.1. Structure and morphology of CPVA microspheres

In this work, CPVA microspheres are regarded as support for the immobilization of aluminum chloride because there are significant



Scheme 1. Chemical structure of CPVA microspheres.

numbers of hydroxyl groups on the surface of CPVA microspheres and dense hydroxyl groups lay a solid foundation for a high loading. A direct cross-linking reaction using glutaraldehyde as cross-linker was performed in a suspension system to prepare CPVA microspheres. The chemical structure of CPVA microspheres can be schematically expressed as Scheme 1.

Fig. 1 gives the SEM image of CPVA microspheres. The sphericity of microspheres is fine, the surface is smooth, and their grain sizes are almost uniform. The CPVA microspheres used in this work have a mean diameter of 160 μm .

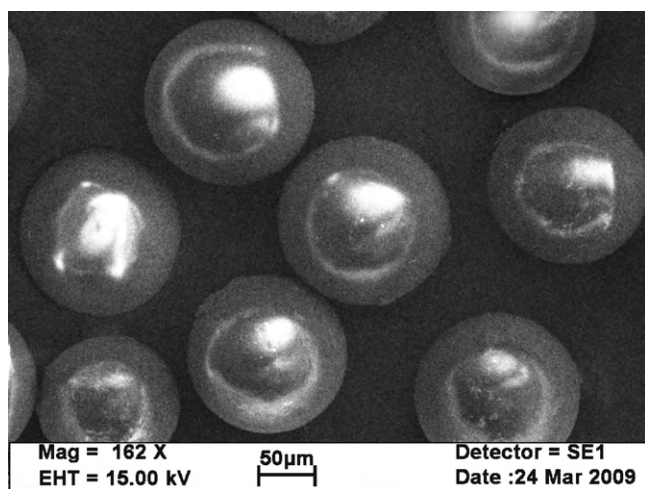


Fig. 1. Scanning electron micrograph of CPVA microspheres.

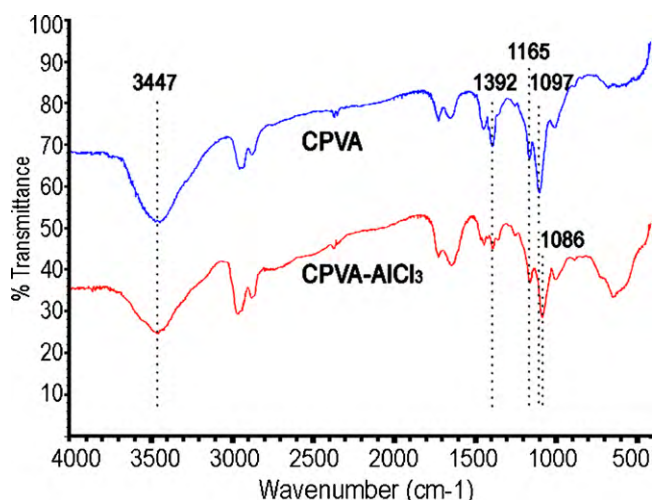


Fig. 2. FTIR spectra of CPVA and CPVA- AlCl_3 microspheres.

In the infrared spectrum of CPVA (Fig. 2), two characteristic bands of O-H groups are present at 3447 cm^{-1} and 1392 cm^{-1} . The former is attributed to the stretching vibration of hydrogen-bonded hydroxyl groups, and the latter is ascribed to the bending vibration of hydroxyl groups. A band at 1097 cm^{-1} is assigned to the stretching vibration of C-O bond of the secondary hydroxyl groups of PVA chains. The stretching frequency of ether bond observed at 1165 cm^{-1} evidences that the PVA chains are cross-linked. These characteristic absorptions and the SEM image can confirm the structure of CPVA microspheres shown in Scheme 1.

3.2. Structure of immobilized Lewis catalyst CPVA- AlCl_3

3.2.1. Infrared spectrum of CPVA- AlCl_3

Fig. 2 shows the infrared spectra of CPVA and CPVA- AlCl_3 microspheres. In the spectrum of CPVA- AlCl_3 , the stretching frequency of C-O bond in secondary hydroxyl groups has shifted from 1097 cm^{-1} to 1086 cm^{-1} , owing to the decreased electron density of C-O bond, and that was caused by the formation of C-O-Al bond (hydrogen chloride gas was also released during the immobilization reaction). In addition, two weakened bands at 3447 cm^{-1} and 1392 cm^{-1} suggest the decreased number of the hydroxyl groups on CPVA microspheres. These spectrum changes indicate that aluminum chloride has been immobilized onto CPVA microspheres via covalent bonding.

3.2.2. Structural change of bound AlCl_3 on CPVA- AlCl_3 microspheres

During AlCl_3 immobilization process, the contents of both Al and Cl elements on CPVA- AlCl_3 microspheres were determined as described previously, and their loadings as a function of time are displayed in Fig. 3. It can be observed that the loadings of both Al

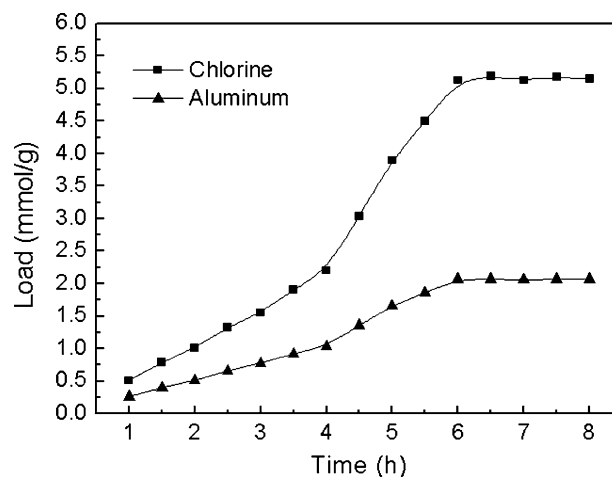
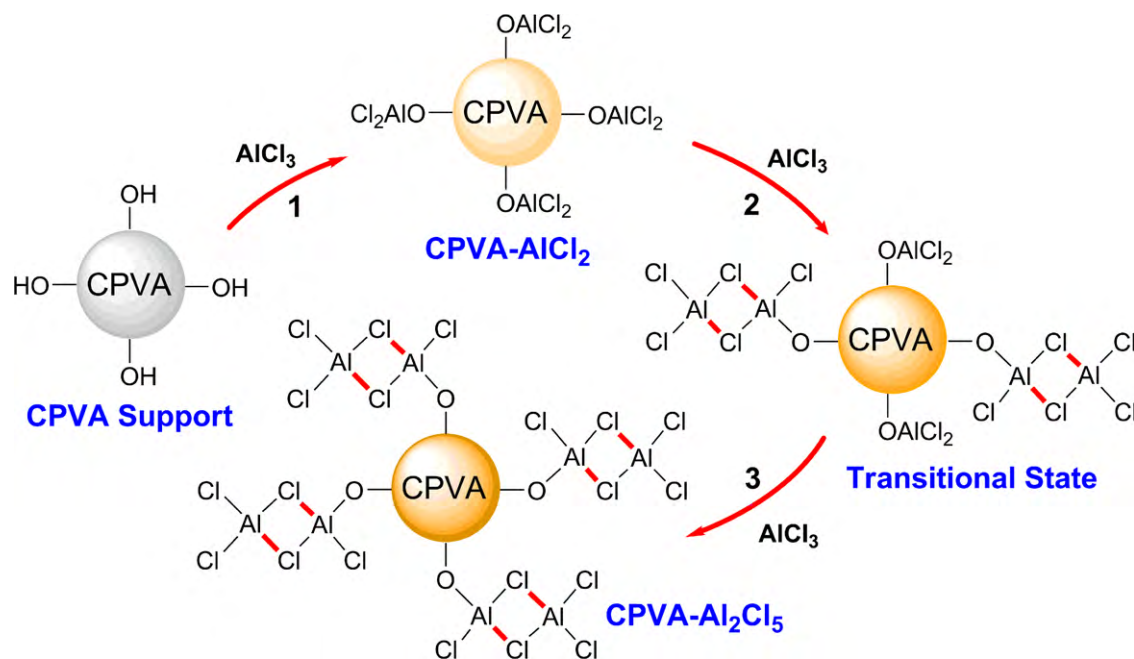


Fig. 3. Variations of loadings of Cl and Al elements on CPVA- AlCl_3 microspheres with time. Temperature: 40°C ; solvent: chloroform.



Scheme 2. Immobilization process of AlCl₃ on CPVA microspheres.

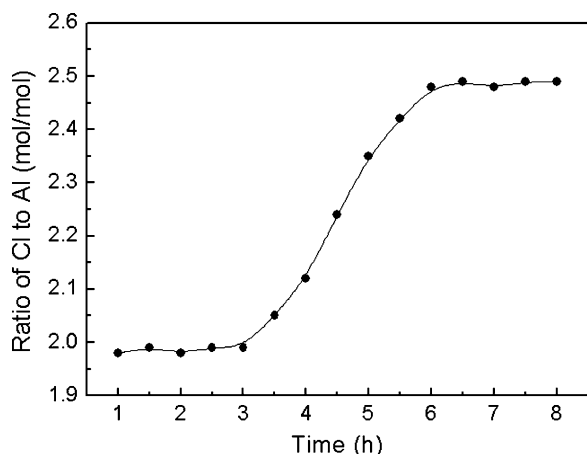


Fig. 4. Variations of the loading ratio of Cl to Al with time.

and Cl elements increased with the reaction time and reached a plateau after 6 h, indicating the increase of the amount of immobilized AlCl₃ with the reaction time at the starting stage and implying a saturated immobilized amount (2.07 mmol/g). More importantly, loading ratios of Cl to Al at varying reaction time were calculated and presented in Fig. 4. It can be found clearly that the ratio is not constant. In 1–3 h, the ratio of Cl/Al remained at a value of circa 2.0, suggesting that the bound AlCl₃ has a form of –AlCl₂; in 3–6 h, the ratio increased from 2.0 to 2.5, indicating that the immobilized AlCl₃ exists in a transition state; after 6 h, the ratio stays around 2.5, implying that the bound AlCl₃ possesses another form of –Al₂Cl₅.

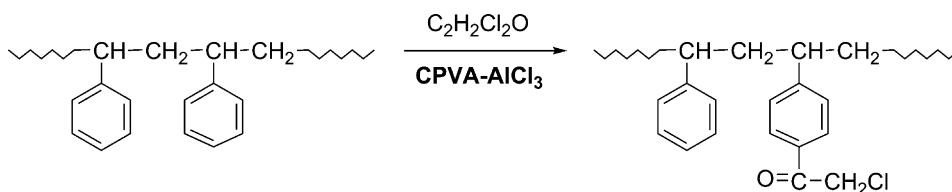
It is known that aluminum chloride exists in organic solvents as a dimer [35]. Based on this fact, the following fundamental points can

be speculated for the immobilization reaction of aluminum chloride. (1) At the starting stage, the immobilization reaction occurred between AlCl₃ and hydroxyl groups, producing –OAlCl₂ groups with the Cl/Al ratio of 2.0. Here, AlCl₃ was being immobilized on CPVA microspheres as a monomeric form of –AlCl₂. (2) While the immobilization of AlCl₃ as a monomeric form reached saturation, free AlCl₃ molecules started to attack the –OAlCl₂ groups, leading to the formation of –OAl₂Cl₅. As a result, the Cl/Al ratio increased with reaction time in the transitional stage. (3) After 6 h, all of the immobilized AlCl₃ existed as the dimeric form of –Al₂Cl₅, and the –OAl₂Cl₅ groups could stably exist on the surface of CPVA–AlCl₃ microspheres so that the ratio no longer changed. It is obvious that the immobilization reaction of AlCl₃ on CPVA microspheres proceeded step by step, and the entire immobilization process of aluminum chloride on CPVA microspheres can be schematically expressed in Scheme 2. With regard to the dimeric form of AlCl₃ on solid supports, Sato et al. also reported a similar finding [36]. They prepared silica-grafted aluminum chloride catalysts by the contact of aluminum chloride vapor with silica surfaces at lower temperatures (below 250 °C), finding that the grafted aluminum chloride had a structure of dimer and possessed a high catalytic activity. In our experiments, the dimeric structure of immobilized AlCl₃ was also observed, but it was formed during the common bonding reaction, moreover, the structural change of bound AlCl₃ can be controlled via controlling the reaction time.

3.3. Catalytic property of CPVA–AlCl₃

3.3.1. Catalytic activity for Friedel–Crafts acylation of polystyrene

The immobilized Lewis acid CPVA–AlCl₃ was used to catalyze Friedel–Crafts acylation reaction (a chloroacylation reaction) of polystyrene. In the electrophilic substitution reaction, as shown



Scheme 3. Chloroacylation reaction of polystyrene.

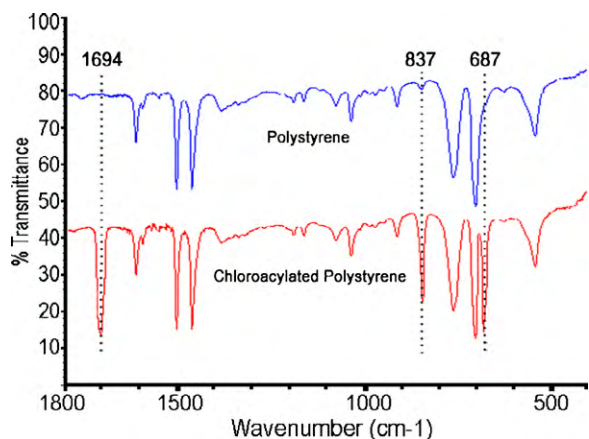


Fig. 5. FTIR spectra of polystyrene and chloroacetylated polystyrene.

in Scheme 3, CPVA- AlCl_3 microspheres acted as heterogeneous catalysts and the hydrogen atom at the para-position of benzene ring was substituted for chloroacetyl group. The infrared spectrum of chloroacetylated polystyrene is presented in Fig. 5. When the spectrum of chloroacetylated polystyrene is compared with that of polystyrene, it can be found that two new bands appear at 1694 cm^{-1} and 687 cm^{-1} . The former should be attributed to the stretching vibration absorption of carbonyl group $\text{C}=\text{O}$, and the latter is ascribed to the stretching vibration absorption of $\text{C}-\text{Cl}$ bond. At the same time, the band at 837 cm^{-1} has been strengthened greatly. It corresponds to the vibration absorptions of $\text{C}-\text{H}$ bond of benzene ring whose hydrogen atoms at the para-position were substituted. The above facts show clearly that polystyrene has been chloroacetylated under the catalytic action of CPVA- AlCl_3 microspheres.

In order to show that immobilized aluminum species were indeed responsible for catalysis, rather than any residual Lewis acid that had leached from the support during the reaction, the catalysts in the reaction were filtered off and the filtrate was analyzed for its aluminum content by atomic absorption spectrometry, which showed a negligible release of AlCl_3 . Also, the filtrate was found to be inactive for the Friedel–Crafts acylation reaction. These observations indicate that CPVA- AlCl_3 microspheres are stable under the reaction conditions, and there is no leaching of acid moieties during the reactions.

Four forms of catalysts – CPVA- Al_2Cl_5 in dimeric form, CPVA- AlCl_2 in monomeric form, CPVA- AlCl_3 in transitional state, and CPVA support – were respectively used in the acylation reaction. The conversions of polystyrene repeating unit are presented in Fig. 6. The results suggest that: (1) CPVA microspheres have no obvious catalysis for this reaction; (2) whatever form of aluminum chloride exists on microspheres, CPVA- AlCl_3 as an immobilized Lewis acid catalyst can effectively play a catalytic role in the Friedel–Crafts acylation reaction of polystyrene; (3) the presence of $-\text{Al}_2\text{Cl}_5$ gives rise to an activity enhancement, and the catalytic activities follow an order: CPVA- $\text{Al}_2\text{Cl}_5 >$ CPVA- AlCl_3 in transitional state $>$ CPVA- AlCl_2 . For the activity difference among three kinds of CPVA- AlCl_3 , it can be explained based on their difference in acidity. On the surface of CPVA- Al_2Cl_5 , there have the most aluminum atoms which can exert an action of accepting electron pairs, so that more carbonium ions will be produced in the electrophilic substitution reaction. It is of great advantage to the Friedel–Crafts acylation reaction, resulting in the highest conversion of the repeating styrene unit of polystyrene.

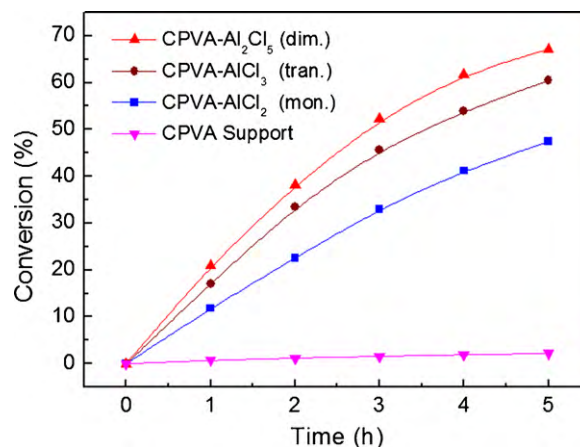


Fig. 6. Conversion of the repeating unit of polystyrene using catalysts with different forms. Added amounts of various catalysts with 10.35 mmol of aluminum loading: CPVA- Al_2Cl_5 (5 g), CPVA- AlCl_3 (7.61 g), and CPVA- AlCl_2 (13.27 g); CPVA support (13.27 g). Temperature: 25°C ; solvent: chloroform.

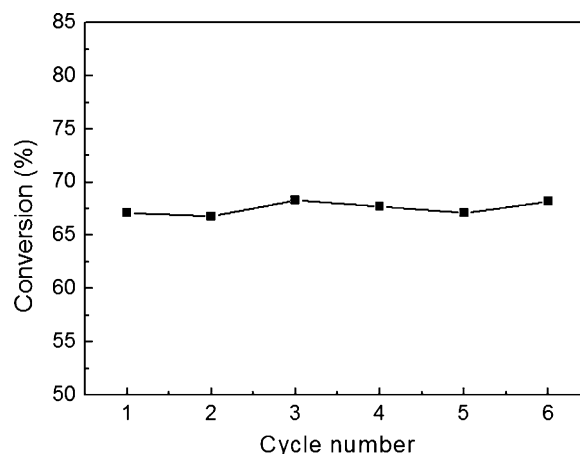


Fig. 7. Conversion of the repeating unit of polystyrene catalyzed by the repeatedly used CPVA- Al_2Cl_5 . Reaction time: 5 h .

3.3.2. Recyclability and reusability of CPVA- AlCl_3

The filtered CPVA- AlCl_3 microspheres were sufficiently soaked and washed with chloroform to remove the adsorbed substances, and then the recycled catalysts were repeatedly used in the Friedel–Crafts acylation reactions of polystyrene under the same reaction conditions. Fig. 7 shows the conversion of polystyrene repeating unit as a function of cycle number by using CPVA- Al_2Cl_5 as the tested catalyst. No significant changes in activity or selectivity were observed over these reaction times, indicating the excellent recyclability and reusability of this solid catalyst.

4. Conclusions

Environmentally friendly catalysis is an important ingredient of green chemistry, and it is also a considerable issue for industrial application. Therefore, we immobilized a typical Lewis acid catalyst, AlCl_3 , onto cross-linked polyvinyl alcohol microspheres via covalent bonding, and obtained an environmentally friendly catalyst CPVA- AlCl_3 . The investigation results suggest that CPVA utilized as the support to immobilize aluminum chloride has comparative advantages of stability and loading capacity. During the immobilization process, the structure of AlCl_3 bound on CPVA microspheres would gradually change from $-\text{AlCl}_2$ (monomeric form) to $-\text{Al}_2\text{Cl}_5$ (dimeric form). CPVA- AlCl_3 has outstanding catalytic activity for the Friedel–Crafts acylation reaction

of polystyrene, and its dimeric species displays a much stronger activity than others. Their catalytic activities follow an order: CPVA- Al_2Cl_5 > CPVA- AlCl_3 in transitional state > CPVA- AlCl_2 . Moreover, this kind of immobilized Lewis acid catalyst has excellent recyclability and reusability, and in particular CPVA- Al_2Cl_5 exhibited an extremely low extent of catalyst deactivation in the repeated acylation reactions. Further in-depth studies concerning the industrial feasibility of CPVA- AlCl_3 should be continued, focusing on some areas such as turnover number, turnover frequency, and particularly activity and stability. In addition, immobilizing boron trifluoride, titanium tetrachloride, stannum tetrachloride, and zinc chloride, on CPVA microspheres to diversify immobilized Lewis acid catalysts is another area of future exploration.

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