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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 ($–AlCl_2$) to the dimeric form ($–Al_2Cl_5$). The presence of $–Al_2Cl_5$ 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.

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 (–$AlCl_2$) to the dimeric form (–Al_2Cl_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 ($Mr = 4.7 \times 10^4$) 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