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Preparation of $AlCl_3$/silica gel catalyst for simultaneously removing thiophene and olefins from coking benzene by inclosed grafting method

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ABSTRACT

$AlCl_3$/silica gel catalysts were prepared by inclosed grafting method in the autoclave and their catalytic activities for alkylation reaction of thiophene with olefins in benzene were studied. The gas chromatograph and chromatography–mass spectroscopy were used to quantitatively determine the thiophene in benzene and qualitatively measure the reaction products, respectively. XPS, SEM, EDX and N_2 adsorption techniques were used to characterize the physical and chemical properties of catalyst samples. The results show that $AlCl_3$ can be effectively anchored by reacting with the silanol groups on silica gel surface to form the $Si_x(OH)_{y-a}O_aAlCl_{(3-a)}$ species and the prepared $AlCl_3$/silica gel catalyst possesses the significant activity for the alkylation reaction of thiophene and olefin. The preparation conditions, such as mass ratio of $AlCl_3$/silica gel support, grafting temperature and time, and thermal treatment temperature of silica gel, have an important role on the content and distribution of active component over silica gel support, and thus affect the catalytic activity. The optimum preparation conditions of $AlCl_3$/silica gel catalyst are that $AlCl_3$ is grafted on silica gel support, which has been thermally treated at 400 °C for 3 h, and at 180 °C for 4 h with the mass ratio of 0.20 for $AlCl_3$/silica gel support. The loading ratio of $AlCl_3$ on silica gel can reach about 64 wt.% and the optimal conversion rate of thiophene in benzene is 94.23% when the ratio of liquid to catalyst is 20 mL/g.

1. Introduction

Benzene, an important chemical raw material, is obtained today mostly from petroleum, but the production of benzene from coal coking has gained considerable importance. However, the benzene obtained by coking industry contains high proportions of olefins and thiophene, which are necessary to be removed to a great extent because of the high purity requirements for benzene used for further processing [1]. Nowadays, to remove the olefins and thiophene impurities, the industrialized processes for the refining of coking benzene include washing with concentrated sulfuric acid [2] and catalytic hydrorefining [3–5]. The disadvantages of these methods mainly are the equipment corrosion caused by concentrated sulfuric acid, the decrease of the benzene yield, the loss of olefins and thiophene and the formation of secondary environmental pollutants that are hard to be controlled [6,7]. However, as the impurities in coking benzene, the olefins (such as 1-hexene, 1-pentylene and styrene) have higher reactive activity with thiophene than benzene. If the olefins and thiophene in benzene can react with each other to produce alkylthiophenes, of which physical and chemical properties are significantly different from those of benzene and thus can be easily separated by the distillation process, the olefins and thiophene can be simultaneously removed, and also the alkylthiophenes can be recycled. To achieve the purpose, the key problem to be solved is to prepare the catalyst with high activity and selectivity for alkylation reaction.

Anhydrous $AlCl_3$ is a well-known homogeneous acidic catalyst for the liquid phase Friedel–Crafts reactions [8] and it is cheaper compared with the acid modified zeolites, such as Hbeta [9], fluorinated Hbeta [10], phosphoric acid loaded MCM-41 [11] and so on. However, its use as a Lewis acid catalyst in some reactions is limited because of difficult separation from the reaction product causing a large volume liquid waste, corrosive nature, high toxicity and no reuse in the subsequent batches [12,13]. So it is required to be anchored on some solid supports, such as SiO_2 [14,15], Al_2O_3 [16], resin [17,18] and zeolite [13,19]. The grafting methods mainly include the gas loaded method [12,20] and the impregnation method [21]. For the gas loaded method, the support in the fixed bed is treated by $AlCl_3$ vapor carried by gas, so it cannot avoid the waste of $AlCl_3$ and takes a long time to complete the grafting process. For the impregnation method, the support is impregnated in anhydrous liquid medium with dissolved $AlCl_3$, for instance, the ether, chloroform, CS_2 and CCl_4, which are all volatile toxic organic substances. Meanwhile, the samples prepared still need to be filtered and calcined. And thus, this method has the disadvantages of environmental pollution and cumbersome preparation steps.

Based on the above, it is necessary to find a feasible method to graft $AlCl_3$ on support with the advantages of high utilization efficiency of $AlCl_3$, no environmental pollution and easy operation. To achieve this

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purpose, the silica gel was selected as the support for its characteristics namely low cost and easily obtainable, and the inclosed grafting method was explored to prepare the $AlCl_3$/silica gel catalyst in an autoclave. The physical and chemical properties of catalysts prepared under different conditions were characterized by XPS, SEM, EDX and N_2 adsorption techniques and the effects of the preparation conditions on the catalytic activity of the $AlCl_3$/silica gel catalyst are also investigated in this paper.

2. Experimental

2.1. Experimental materials

Benzene (Tianjin Guangfu Fine Chemical Research Institute, 99.9%), thiophene (Alfa Aesar, 99%), 1-hexene (Alfa Aesar, 98%), anhydrous $AlCl_3$ (Xiya Ltd., 99.5%) and spherical silica gel with the diameter range of 1.5–2.5 mm (Qingdao Makall Ltd.) are all purchased from the commerce.

2.2. Preparation of $AlCl_3$/silica gel catalysts

Before being used as the catalyst support, the commercial silica gel was thermal treated in a muffle for 3 h, and then cooled in a dryer. The scheme of the device for $AlCl_3$/silica gel catalyst preparation is shown in Fig. 1. The anhydrous $AlCl_3$ was put on the bottom of the autoclave with a teflon liner, and the 10 g silica gel support was put in the teflon support, on which there are lots of pores with the diameter of 1.0 mm. After being sealed, the autoclave was put in a muffle at different temperatures (grafting temperatures) for different grafting times. Then it was taken out and cooled, and the catalyst can be obtained. By the way, the grafting temperature is in the range of 180–240 °C, which is higher than the sublimation temperature of the anhydrous $AlCl_3$ (178 °C), so the solid $AlCl_3$ will be turned into vapor phase. The major characteristics of this method lie in its high load amount of $AlCl_3$ on support and no escape of caustic $AlCl_3$ during the preparation of catalyst. The mass ratio (R) of anhydrous $AlCl_3$/silica gel support and the active component content of the $AlCl_3$/silica gel catalyst (M_{ac}, wt.%) are respectively calculated as follows by Eqs. (1) and (2).

$$R = \frac{m_{ac}}{m_0} \tag{1}$$

$$M_{ac} = \frac{m - m_0}{m} \times 100\% \tag{2}$$

where, m_{ac} is the mass of the anhydrous $AlCl_3$ (g); m_0 is the mass of the silica gel support (g); and m is the mass of the $AlCl_3$/silica gel catalyst prepared (g).

2.3. Activity evaluation of catalysts

The alkyl reaction of thiophene with olefin was carried out in a simulative coking benzene solution with the thiophene concentration of 704.5 mg/L and the molar ratio of 1-hexene to thiophene of 6:1. In the experiment, 2.5 g $AlCl_3$/silica gel catalyst was put into a 50.0 mL simulative coking benzene solution in a flask, which was emerged in the silicone oil thermostat system at 60 °C for 4 h under the condition of magnetic stirring. After the reaction, the concentration of thiophene in the solution and the reaction products were respectively quantitatively determined and qualitatively measured by gas chromatographs with a flame photometric detector (GC-FPD) and chromatography–mass spectroscopy (GC–MS). The conversion rate of thiophene ($\eta_{thiophene}$, %) was calculated by Eq. (3), and the value of $\eta_{thiophene}$ was an indicator to determine the level of the catalytic activity of $AlCl_3$/silica gel catalyst.

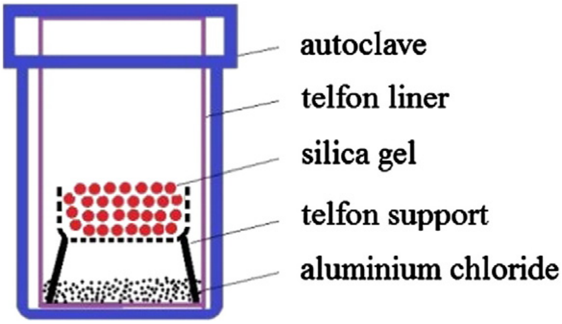

Fig. 1. Scheme of the device for the $AlCl_3$/silica gel catalyst preparation.

$$\eta_{thiophene} = \frac{c_o - c}{c_o} \times 100\% \tag{3}$$

where, c_o is the initial concentration of thiophene in the solution (mg/L); and c is the concentration of thiophene in the solution (mg/L) after the reaction.

2.4. Characterization of catalysts

The structure of samples was characterized by X-ray diffraction (XRD) apparatus of Rigaku D/max-2500 made in Japan at a scanning rate of 5°/min from 5° to 85° with Cu-Kα radial, $\lambda = 0.154$ nm X-ray, 40 kV tube voltage and 100 mA tube current. The surface area of the silica gel support and $AlCl_3$/silica gel catalyst derived from nitrogen adsorption isotherms was measured with the SORPTOMATIC 1900 Series instrument, with the use of BET methods. The surface morphology of the catalyst and the alumina content of the grafted silica samples were respectively characterized by scanning electron microscopy and energy-dispersive X-ray spectroscopy (EDS) with a JEOL JSM-6700F scanning electron microscope with an accelerating voltage of 10 kV.

In order to investigate how the anhydrous $AlCl_3$ was grafted on the silica gel support, the binding energy of O 1s and Si 2p on the surface of silica gel before and after grafting $AlCl_3$ was compared. The binding energy was determined by X-ray photoelectron spectroscopy (XPS)

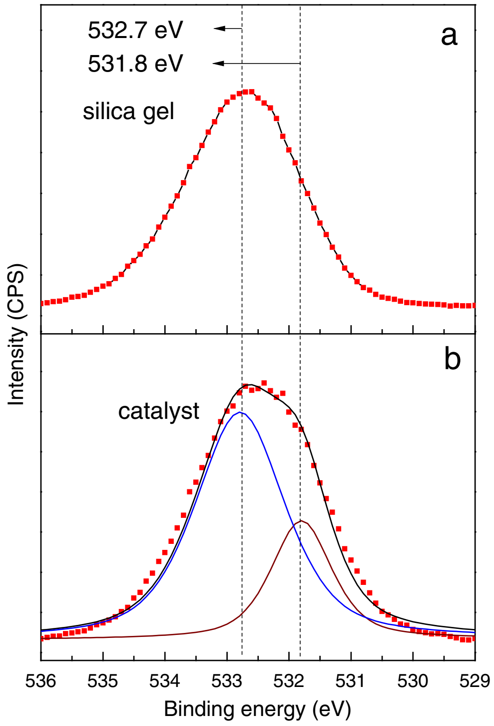

Fig. 2. XPS spectra of the core level of O 1s region recorded with silica gel (a) and the $AlCl_3$/silica gel catalyst (b) prepared at 180 °C.