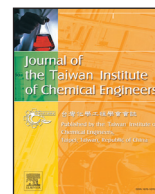




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Mesoporous alumina modified calcium catalyst for alcoholysis of polycarbonate

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ABSTRACT

Calcium-functionalized mesoporous γ -alumina was synthesized for alcoholysis of Polycarbonate (PC). Compared with the traditional homogeneous depolymerization process, such alcoholysis process presents a higher capacity, more time effective and environmental benign. Benefited from such mild condition, the operation can be continuously performed without any equipment corrosion occurring. Such mesoporous γ -alumina composite can be synthesized in one step sol-gel method by utilizing aluminium isopropoxide, calcium nitrate as basic precursors and Pluronic P123 as a structure directing agent. One-pot method can effectively avoid the loss of active components namely Ca species in comparison to conventional impregnation method. As for the reasons leading to such great degradation efficiency, one is the strengthened basicity supplied by the introduction of Ca species, the other is the typical mesoporous nanostructure which is beneficial for improving the kinetic driving force, in other words, the synergistic effects make the superior work efficiency for PC degradation. The operation conditions were optimized including the molar ratio of Ca/Al, temperature, methanol and tetrahydrofuran (THF) dosage and Ca-Al₂O₃ dosage. Under such optimum conditions, the conversion of PC was approximately 100 wt.%. The catalyst endures a long recycle without any obvious inactive tendency as well as remained mesoporous structure. The transesterification kinetic behaviors were also investigated with an activation energy of 153 kJ/mol. In addition, a plausible catalysis mechanism for the methanolysis of PC was proposed.

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1. Introduction

With high impact strength, strong heat resistance and excellent electrical and optical properties, Polycarbonate (PC) causes long-term environment, economic and waste disposal problems requiring emergent treatment [1]. Great efforts were made to deal with PC [2,3], among them one of the most promising avenue is depolymerization through a chemical treatment to obtain starting material such as bisphenol A (BPA) and Dimethyl carbonate (DMC). Various methods for the chemical recycling of waste PC to restore the monomers such as pyrolysis [4,5], alcoholysis [6,7] and hydrolysis were developed [8,9]. In such homogeneous catalysts involved process, except the serious environmental and corrosion problems caused by the strong bases (such as alkali metal hydroxides) or the destructive H₂SO₄ [10–14], the hard recycle problem and the harsh operation temperature yet restrict their application to some extent.

As regard to these issues, new type catalysts were exploited in order to solve these issues [15–21].

Mesoporous catalyst is extremely desirable serving as the catalyst in environmentally benign processes because they can catalyze different types of reactions under relatively moderate conditions. Considering the alcoholysis of PC occurring is more favorable at basic sites, the mesoporous nanostructure endurable to alkaline is a great demand. Consequently many researchers have been made to prepare mesoporous solid bases [22–24]. The mesoporous texture is beneficial to speeding the reaction kinetic behaviors. For instance, by means of impregnating alkali metals, alkaline-earth metals and transition metals into mesoporous supports such as mesoporous SiO₂ [25,26], Al₂O₃ [27,28], ZrO₂ [29,30], the basicity of catalysts is dramatically enhanced under the premise that scarcely destroy structure of the matrix. In contrast to SiO₂ and ZrO₂, Al₂O₃, especially that of the γ -type, is an excellent support for a majority of solid superbases [31,32], which means the occurrence of mesoporous Al₂O₃ offers a good track to fabricate mesoporous solid superbase [27].

Besides, the large initial aspect ratio is beneficial to creating more contact area between PC solution and the catalyst. The

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alloyed catalyst is a good choice due to the deficiency of basic intensity for a single catalyst. Compared with catalysts by impregnating active center into supports, which is limited by the complex preparation technology, higher energy consumption, and the poor precise control of loading content, it is highly desirable to design a time efficient and energy conservative one pot synthesis system. This strategy allows the synthesis and modification of mesoporous alumina in a one-pot process, avoids post-treatment framework damage, and saves time and energy.

Based on the above mentioned points, the wormhole-like calcium-functionalized mesoporous γ -alumina was prepared via one-pot energy conservative synthesis path. Such alloyed catalyst has a large initial aspect ratio and a well ordered framework which enables a well mass transfer process. The alcoholysis of Polycarbonate (PC) in the presence of the mesoporous Ca-Al₂O₃ was investigated. Benefit from the enhanced basic strength provided by Ca species and the typical large initial ratio, the mesoporous Ca-Al₂O₃ exhibits excellent catalytic activity and reusability in reaction, which means that the corporation of Ca and Al₂O₃ may open up a route for the design and synthesis of new functional materials.

2. Experiments

2.1. Materials

Pure PC pellets (3 mm length and 2.5 mm diameter with MW about 20,000) were used as model plastics, triblock copolymer P123 (EO₂₀PO₇₀EO₂₀, M_{av} = 5800, Aldrich) as structure directing agent, aluminium isopropoxide (AIP, CP) as aluminium source, hydrochloric acid (HCl, 37wt%, AR) and nitric acid (HNO₃, 68wt%, AR) as pH adjusters, Calcium Nitrate Tetrahydrate (Ca(NO₃)₂•4H₂O, AR) as Ca²⁺ precursor, and deionized water (H₂O) as dissolving media, Methanol (AR) was purchased from BASF, Tetrahydrofuran (THF) and Sodium hydroxide (NaOH) were provided by Damao chemical reagent factory in Tianjin.

2.2. Synthesis procedure

The mesoporous CaO-Al₂O₃ was prepared via sol-gel method in aqueous solution. In a typical synthesis, a certain amount of aluminium isopropoxide (AIP) and calcium nitrate tetrahydrate (Ca(NO₃)₂•4H₂O) was dissolved in distilled water and stirred at 80 °C for 2 h, and then nitric acid (HNO₃) was added into above-mentioned solution and kept on stirring at 80 °C for 2 h (solution A). Meanwhile, P123 was added into deionized water containing hydrochloric acid (HCl) and stirred at 40 °C for approximately 4 h so that P123 was dissolved completely (solution B). Mixing solution A and B, and continually stirring for 12 h at 40 °C. The transparent sol was obtained. The molar composition of the synthesis solution was AIP: Ca(NO₃)₂•4H₂O: P123: H₂O: HCl: HNO₃ = 1: x(0.05, 0.10, 0.15): 0.01: 173: 2.4: 0.76. The resulting milky white mixture was obtained by slowly adjusting pH of transparent sol to around 9 with NaOH, and placed in air for 2 days. The digested gel was filtered and simultaneously washed with deionized water, then dried in the oven at 373 K overnight, and followed by calcination at a

2.3. Catalyst characterization

X-ray powder diffraction patterns of the samples were conducted on an XB-3A instrument rendering monochromatic Cu-K α radiation (λ = 0.15418 nm), with a step size of 0.02° and 0.05° in the low-angle (0.5° – 10°) and wide-angle (10° – 80°) range, respectively. The N₂ adsorption/desorption isotherms were finished in Quantachrome Instruments autosorb iQ2 at 77 K. The samples must be pretreated in situ under vacuum at 573 K. The surface area was calculated according to BET method, whereas the volume and diameter of mesopores were determined by BJH method. CO₂-TPD was recorded via a Thermo Electron Corporation TPD/R/O1100 series catalytic surface analyzer equipped with a TCD detector. The samples were heated to 800 °C and the heating rate of is 10 °C/min with He pumping (20 ml/min). The products needs the adsorption of CO₂ at room temperature for 30 min before the CO₂-TPD test. IR spectra were performed using a Nicolet 510P FT-IR spectrometer in the range of 4000–400/cm, using KBr powder containing ca.1 wt.% of sample. Particle morphologies were tested using a transmission electron microscope (TEM) (JEM-2100). The samples were ultrasonically dispersed in ethanol and then dropped onto carbon films on copper grids to conduct the TEM characterization.

2.4. Alcoholysis of PC

The mixture of PC (5 g), methanol, tetrahydrofuran (THF) as dissolving media and catalysts (w_1) was added into an autoclave (100 ml) with a magnetic rotor and thermometer. The system was heated up in heating magnetic stirrer to the given temperature and reacted for certain time at autogenous pressure (0–1 MPa). After reaction, the autoclave with resulting mixture was cooled down in condensate water to room temperature. The mixture (w_2) of unreacted PC and catalysts was separated from residue by suction filtration. The obtained filtrate mainly composed of THF, residual methanol, soluble PC of different degree of polymerization, product BPA and DMC was treated by vacuum distillation to separate THF, methanol and DMC as distillate from soluble PC and BPA as residue. Afterwards, the residue containing soluble PC of different degree of polymerization and BPA was dissolved with 20 ml methanol and put at room temperature overnight. PC (w_3) with higher degree of polymerization were precipitated owing to insolubility in methanol and filtered out. Product BPA (w_4) was obtained by vacuum distillation from filtrate. Finally, the residual was characterized by FT-IR.

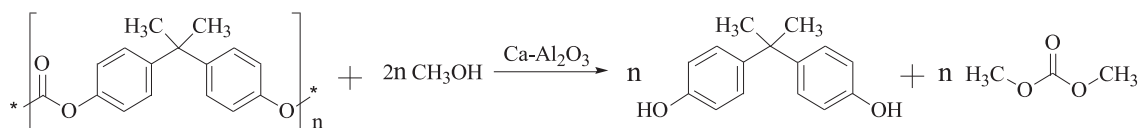
Conversion of PC and yield of BPA were calculated by following equation:

$$\text{Conversion of PC} = \frac{5 - (w_2 - w_1 + w_3)}{5} \times 100\%$$

$$\text{Yield of BPA} = \frac{W_4}{5} \times \frac{M(\text{PC})}{M(\text{BPA})} \times 100\%$$

M (PC) and M (BPA) are the molar masses of the repeating unit of PC and BPA, respectively.

The reaction formula was as follows:



ramping rate of 5 °C/min from room temperature to 823 K in air for 5 h.

n is the degree of polymerization.

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