

Study on catalytic pyrolysis of polystyrene over base modified silicon mesoporous molecular sieve

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Received 26 August 2007; received in revised form 22 October 2007; accepted 24 October 2007

Available online 30 October 2007

Abstract

K₂O/Si-MCM-41 molecular sieve was prepared by impregnating Si-MCM-41 with KNO₃. The obtained material was characterized by XRD, FT-IR, TEM and N₂Ad/De, the results indicated that K₂O/Si-MCM-41 was of typical mesoporous structure, and the long-range order of K₂O/MCM-41 became poorer with the increase of K₂O. The catalytic properties of K₂O/Si-MCM-41 were investigated in the pyrolysis of polystyrene (PS). The results were compared with those obtained using CaO, Si-MCM-41 and Al-MCM-41 as catalysts. It was shown that K₂O/Si-MCM-41 is of better catalytic activity. The effect of preparing conditions on activity of K₂O/Si-MCM-41 was discussed. KNO₃ was almost completely decomposed into K₂O at optimum calcination temperature of 600 °C. Under the optimum conditions of mass percentage of K₂O 9%, temperature 400 °C, *m*(catalyst):*m*(PP) = 0.02 and reaction time 0.5 h, the conversion of PS was 90.53%, the yield of liquid products was 85.67%, and the yield of styrene reached 69.02%.

Published by Elsevier B.V.

Keywords: Mesoporous molecular sieves; Polystyrene; Catalytic pyrolysis; Styrene

1. Introduction

The amount of waste plastic discarded each year is constantly increasing and is causing serious pollution problems. The low biodegradability of polystyrene (PS) creates a serious environmental problem that is directing the governments to propose a solution to solve it based on source reduction, reuse and recycling. If this material can be chemically recycled, it will become a cheap and abundant source for useful chemicals and energy. Among various recycling methods, the chemical method which converts waste plastics to useful hydrocarbons has been recognized as a promising approach [1–4]. PS can be depolymerized to monomer styrene, which can be polymerized

to polystyrene again and be widely used to synthesize other chemicals. It is known that waste PS can be converted into styrene by simple thermal degradation at 873 K, but the yield is poor [5–7]. By using suitable catalysts, the degradation temperature can be lowered with a higher yield of styrene monomer [8–10]. The solid base is of good catalytic activity for catalytic degradation of PS [11–13]. Both the degradation rate and the selectivity of styrene can be enhanced. This is partially because the rate determining step of PS degradation is the elimination of hydrogen atoms to generate carboanions. Accordingly, the role of base sites is to generate carboanions at the initial stage in order to accelerate the depolymerization of PS, and accelerate the cracking of the β-chain to produce styrene. The common used solid base catalysts were salts or oxides of metals [14], and Al₂O₃ and zeolites were usually used as support [15,16]. However, the catalytic cracking of PS over above-mentioned amorphous materials or zeolites as sup-

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port is limited by strong steric hindrances, due to both the bulky nature of PS and the small size of the zeolite micropores. Therefore, it is important to develop a new basic material with excellent catalytic activity and large aperture. It is known that mesoporous MCM-41 materials possess a hexagonal arrangement of uniformly sized unidimensional mesoporous and large surface areas. These exciting properties make them efficient for reactions of larger substrates [17–22]. However, strong base material used to modify MCM-41 can react with silicon, which leads to the collapse of mesoporous structure [23]. For this reason, there is little literature about using MCM-41 as support for basic catalysts. Strong basic site can appear and the destruction to zeolite structure can be avoided when zeolite was loaded by using weak or middle basic materials as base precursors and was properly treated [24]. Therefore, $K_2O/Si-MCM-41$ molecular sieve was prepared by impregnating Si-MCM-41 with KNO_3 in this paper. The obtained material was characterized by XRD, FT-IR, TEM and N_2 Ad/De. $K_2O/Si-MCM-41$ was used as catalyst for pyrolysis of PS. The results were compared with those obtained using CaO, Si-MCM-41 and Al-MCM-41 as catalysts. The effect of preparing conditions, such as K_2O content and calcination temperature, on the activity of $K_2O/Si-MCM-41$ was discussed.

2. Experimental

2.1. Catalyst preparation

Si-MCM-41 was synthesized by hydrothermal method following the procedures reported in previous paper [25]. The mole ratio of the reactants was 0.67 Na_2SiO_3 :1 Silica gel:0.20 CTMABr:102 H_2O .

Si-MCM-41 was impregnated by 0.05, 0.15 or 0.25 mol/L KNO_3 , respectively for 50 min, then the sample was filtrated, dried at 70 °C for 12 h and calcined at 550 °C for 3 h to prepare $K_2O/Si-MCM-41$.

2.2. Catalytic properties test

The catalytic cracking reactions of PS were preformed in a reactor at 400 °C and atmospheric pressure with N_2 flow rate of 15 ml/min. The mixture of catalyst and PS (2:100; w/w) was added into the reactor and heated to 400 °C in 15 min, which was kept constant for a period of 30 min. The liquid and gaseous products coming out from the reactor were separated in a condenser and accumulated to determine their composition by gas chromatography. The reaction products were analyzed on a gas chromatograph with DB-5 glass capillary column of 50m and HP 5890-HP 5989 A GC-MS. FID was used as detector.

2.3. Characterization

X-ray powder diffraction patterns of the samples were obtained on an XB-3A instrument using monochromatic

Cu K_α radiation (λ 0.15418 nm). It was operated at 40 kV and 100 mA. The experimental conditions correspond to a step width of 0.02° and scan speed of 2°/min. It should be noticed that the diffraction must be operated at narrow seam and diffraction region $2\theta = 2-70^\circ$. IR spectra were recorded using a Nicolet 510P FT-IR spectrometer in the range of 2000–800 cm^{-1} , using KBr powder containing ca. 1 wt% of sample. The surface area was calculated using the BET method based on adsorption data in the partial pressure (P/P_0) range 0–0.1 and the pore diameter and pore volume were determined from the amount of N_2 adsorbed at $P/P_0 = 1$ using BJH method. For analysis in the transmission electron microscope (TEM), the samples were crushed under deionized water and dispersed on a holey carbon copper grid. TEM was recorded with a JEM-1200EX electron microscope operated at 100 kv.

3. Results

3.1. Characterization

The IR spectra of $K_2O/Si-MCM-41$ at different calcination temperature were showed in Fig. 1. Spectra *a* exhibits an absorption band at 1384 cm^{-1} corresponding to NO_3^- . With the increase of calcination temperature (400–600 °C), this band becomes much weaker in spectra *b*, which means that KNO_3 was almost completely decomposed at 600 °C. The characteristic bands of NO_2^- at 1550 cm^{-1} and 1364 cm^{-1} are not observed in IR spectra, which means that KNO_3 was decomposed into K_2O not KNO_2 [26]. In the IR spectra, the asymmetric and symmetric stretching vibration bands of framework Si–O–Si appeared at about 1091 and 804 cm^{-1} [27].

Fig. 2 shows the powder X-ray diffraction patterns of Si-MCM-41 and $K_2O/Si-MCM-41$. It can be noted that Si-MCM-41 exhibits the typical hexagonal lattice corresponding to that reported by Beck et al. [25]. After introducing

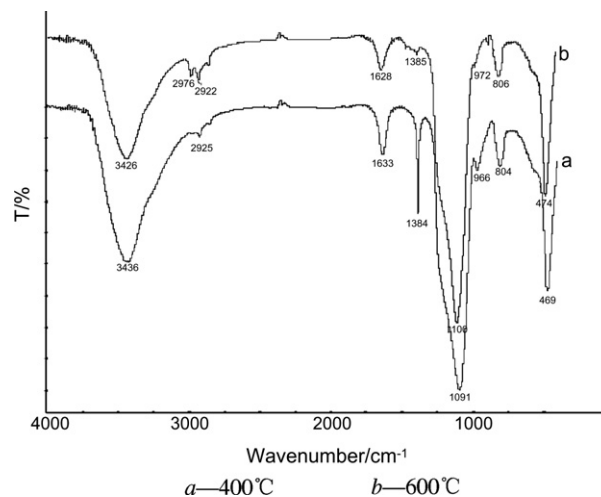


Fig. 1. FT-IR spectra of $K_2O/Si-MCM-41$ at different calcination temperature.

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