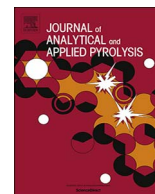




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journal homepage: www.elsevier.com/locate/jaapLight olefin production from catalytic pyrolysis of waste tires using nano-HZSM-5/ γ -Al₂O₃ catalystsZhuangzhang He^a, Qingze Jiao^{a,b}, Zhuqing Fang^a, Taotao Li^a, Caihong Feng^a, Hansheng Li^a, Yun Zhao^{a,*}^a School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, PR China^b School of Materials and Environment, Beijing Institute of Technology, Zhuhai, Guangdong 519085, PR China

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ABSTRACT

Nano-HZSM-5/ γ -Al₂O₃ composite catalysts were prepared by employing mesoporous γ -Al₂O₃ as supports. Their structures, morphologies and acidity were characterized using powder X-ray diffraction (XRD) analysis, Fourier transform infrared spectroscopy (FTIR) analysis, N₂ adsorption and desorption measurement, scanning electron microscope and the NH₃ temperature-programmed desorption. Nano-HZSM-5 was uniformly dispersed and grown on the surface of γ -Al₂O₃ carrier. Nano-HZSM-5/ γ -Al₂O₃ also showed a proper acidity with the uniform acid density distribution. The catalytic pyrolysis of waste tires was carried out in a micro-reactor system, and the composition of the product was analyzed on-line by gas chromatography. The selectivity to light olefins of nano-HZSM-5/ γ -Al₂O₃ reached 29.9%, which was higher than that of nano-HZSM-5 zeolites, γ -Al₂O₃ and the mixture of nano-HZSM-5 and γ -Al₂O₃ with the same composition as nano-HZSM-5/ γ -Al₂O₃.

1. Introduction

The rapid increase of cars and trucks leads to huge amounts of waste tires every year around the world. As non-biodegradable materials, waste tires have hazardous effects on the environment and human beings. Therefore, recycling or reutilization of waste tires has received significant attention. Pyrolysis is considered to be an effective choice to manage waste tires [1,2], and kinds of technologies have been used for tires pyrolysis. For example, conical spouted bed reactors [3–6] show high heat and mass transfer and short gas residence time for volatiles of tires pyrolysis. Fixed beds [7–9] involving a simple process have been widely used for tires pyrolysis. Fluidized bed reactors [10–12] exhibit the earliest implementation of whole tires pyrolysis successfully [13]. Screw kilns [14] can ensure thorough mixing of waste tires, residence times of waste tires can be easily adjusted and waste tires can be fed either in batches or continuously [15].

In general, the products of waste tires pyrolysis can be separated into liquid, gas and solid char. Light olefins are one of the fractions from the pyrolysis products of waste tires. As is well known, olefins especially light olefins are the important basic organic chemical raw materials. Currently, light olefins production mainly come from steam crackers and refinery fluid catalytic cracking unit of petroleum [16]. However, we are facing the problem of petroleum reserve depletion. It is necessary to search for a new resource. Meanwhile, the increasing

amount of waste tires produced annually is a kind of important resource.

Many studies have shown that pyrolysis of waste tires produces not only the valuable oil but also a high yield of gaseous product [17,18]. However, the gas products are mainly been studied for its application as combustion gas rather than for light olefins sources because of the low yield. Whereas the oils contain a lot of polycyclic aromatics and sulfur, thus they can't be used as fuel [19]. Therefore, solid acid catalysts have been applied in many studies for upgrading the quality and quantity of the products obtained from waste tires pyrolysis [20–22]. J. Shah et al. [23] found that a mixture of catalyst (Al₂O₃:SiO₂) gave the equal concentration of aliphatic (35%) and polar (35%) hydrocarbons in oil. SerminÖnenc et al. [24] reported that co-pyrolysis of oily wastes with scrap tires using a ReUS-Y faujisite type catalyst could be an environmentally friendly way for the transformation of hazardous wastes into valuable products.

However, most of the previous research aims at achieving an increase in the yield of single ring aromatics, the gas composition and the quality of the oil from catalytic pyrolysis of waste tires, few researchers have addressed the problem of the production of olefins, especially the light olefins. Chaiyaporn Witpathomwong et al. [25] studied the activity and selectivity of MCM-48 and Ru/MCM-48 for waste tires pyrolysis. The use of Ru/MCM-48 catalyst produced light olefins twice as much as the non-catalytic pyrolysis. Sirirat Jitkarnka et al. [26]

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investigated the catalytic activity of MCM-41 and Ru/MCM-41 for waste tires pyrolysis. The presence of catalysts strongly influenced the yield and nature of products, and 4 times higher of light olefins than non-catalytic pyrolysis could be achieved for Ru/MCM-41 catalysts. However, the yield of light olefins is only 5–8%, which is still low. Furthermore, these researches ignore the yield of C₄ olefin, which is an important part of light olefins in catalytic pyrolysis of waste tires.

HZSM-5 zeolite is used in catalytic pyrolysis of waste tires due to its outstanding properties such as adjustable acidity, hydrothermal stability, and flexibility for catalytic cracking [7,20,27,28]. However, it is not very effective for macromolecular waste tires because of the small size of the channels (less than 0.8 nm) and cavities (typically < 1.5 nm), which imposes diffusional limitations on reactions that could cause high back pressure on flow systems [29–33]. On the other hand, in reactions with large-sized molecules, the small size of the channels and cavities in HZSM-5 would limit the reactants to enter into the cavities for catalytic pyrolysis, the active sites within the channels and cavities can't be fully utilized. In order to increase the yield of light olefins from catalytic pyrolysis of waste tires, HZSM-5 should be modified. Nano-HZSM-5 with a small size exhibit a short-length diffusion path relative to the micron zeolites, which allow the molecules to easily diffuse in or out of the cavities of zeolites resulting in a higher efficiency and a lower deactivation rate for catalytic processes [34]. Therefore, smaller zeolite particles would be better for catalytic pyrolysis of waste tires. However, pure nano-HZSM-5 is still not an ideal catalyst for catalytic pyrolysis of macromolecules due to its micropores. In the catalytic pyrolysis of high density polyethylene, M. Artetxe et al. [35] found that the zeolite (25%) agglomerated by wet extrusion with bentonite (30%) and inert alumina (45%) as catalysts could obtain a high yield of light olefins, because the agglomeration generates mesopores and macropores in the catalyst particles. Therefore, the introduction of mesoporous and macroporous materials into nano-HZSM-5 catalyst is a good choice.

In this work, nano-HZSM-5 with short micropore channels was combined with mesoporous γ -Al₂O₃ to obtain nano-HZSM-5/ γ -Al₂O₃ composite catalysts. Nanoscale HZSM-5 could allow the molecules to diffuse easily in or out of the zeolite channels resulting in a higher efficiency and reduce the secondary reaction of the catalytic pyrolysis products. Mesoporous γ -Al₂O₃ with larger pore size is conducive for macromolecular reactants to enter into the cavities. Moreover, HZSM-5 nanoparticles are uniformly dispersed on the surface of γ -Al₂O₃ with a proper acidity, which overcomes the shortcomings of nanoscale HZSM-5 easy to aggregate and reduces the secondary reaction due to excessive acid density. Therefore, more target products might be obtained. In fact, the selectivity to light olefins of nano-HZSM-5/ γ -Al₂O₃ reached 29.9%, which is higher than that of nano-HZSM-5 zeolites, γ -Al₂O₃ and the mixture of nano-HZSM-5 and γ -Al₂O₃ with the same composition as nano-HZSM-5/ γ -Al₂O₃.

2. Experimental

2.1. Materials

All the chemicals were of reagent grade, used without further purification. Tetrapropylammonium hydroxide (TPAOH, 1 M in water) was purchased from Shanghai McLean biochemical technology Co., Ltd. Tetraethylorthosilicate (TEOS) and sodium aluminate (NaAlO₂) were obtained from Sinopharm Chemical Reagent Co., Ltd., ammonium chloride (NH₄Cl) was purchased from Beijing Chemical Works, and gamma alumina (γ -Al₂O₃) was obtained from Tianjin Chemwit Technology Co., Ltd. Waste tires powders with a size of 0.5–2.0 mm are the used passenger car tires. They were provided by Zhejiang Sheng Jie Rubber Co., Ltd. The ultimate analysis was performed on an Elementar Vario MACRO cube elemental analyzer and the proximate analysis refer to the industrial analysis of coal. The proximate and ultimate analysis of the waste tires are shown in Table 1.

Table 1

The proximate and ultimate analysis of the waste tires.

| | ultimate analysis | | | | | proximate analysis | | | |
|---------------|-------------------|-----|-----|-----|-----|--------------------|------------------|------|--------------|
| | C | H | N | O | S | Moisture | Volatiles matter | Ash | Fixed carbon |
| Content (wt%) | 83.0 | 5.9 | 0.6 | 2.4 | 1.8 | 0.84 | 56.10 | 6.17 | 36.89 |

2.2. Preparation of nano-HZSM-5/ γ -Al₂O₃

NaAlO₂ was dissolved in TPAOH under stirring at room temperature, TEOS was then added drop-wise into the above solution. The mixture was homogenized by stirring for 0.5 h, then kept at 80 °C for 1 h, and finally cooled down to room temperature under magnetic stirring for another 20 h. γ -Al₂O₃ was then added under stirring at room temperature for 0.5 h. The final homogeneous mixture was transferred into a teflon-lined stainless steel autoclave to allow for the hydrothermal reaction at 180 °C for 48 h. The sol-gel solution with a molar composition is 2 Na₂O:2 Al₂O₃:100 SiO₂:25 TPAOH:1157 H₂O. Then the solid product was collected, centrifuged, and washed with deionized water, dried in air over night, and then calcined at 550 °C for 6 h in air. As-synthesized Na-ZSM-5/ γ -Al₂O₃ was treated with a 1.0 mol L⁻¹ NH₄Cl solution for 2 h and three times, and then centrifuged, washed, dried, and calcined in air at 550 °C for 4 h to obtain nano-HZSM-5/ γ -Al₂O₃.

For comparison, nano-HZSM-5 was synthesized using the similar process without introduction of γ -Al₂O₃.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) analysis was obtained on an Ultima IV X-ray diffractometer system (40 kV, 150 mA) using a Cu K_a radiation source, the samples were scanned with a rate of 20° min⁻¹ over 2 θ range of 5–80°. Fourier transform infrared spectroscopy (FTIR) analysis was carried out on a Shimadzu IRAffinity-1s with a resolution of 4 cm⁻¹ and scanning range from 4000 to 400 cm⁻¹. N₂ adsorption and desorption measurement was performed on a BELSORP-MAX specific surface area and pore structure analyzer at 77 K. Samples were out-gassed at 573 K for 3 h. The total surface area was estimated according to the BET method, based on p/p₀ data in the range of 0.05–0.35. The non-local density functional theory (NLDFIT) model was used to obtain the pore size distribution and total pore volume of the samples. The size and morphology of the samples were determined from the scanning electron microscope (SEM) recorded using a JSM-7500F instrument. The acid properties of the four samples were determined by NH₃ temperature-programmed desorption (NH₃-TPD) carried out on a TP-5076 TPD/TPR dynamic adsorption instrument. 100 mg sample was first pre-treated at 600 °C for 1 h with a N₂ flow of 30 mL min⁻¹, and then cooled to 100 °C. NH₃ adsorption was performed using an ammonia flow of 15 mL min⁻¹ for 30 min. N₂ was introduced to remove the physically adsorbed NH₃ for 2 h at 100 °C. NH₃-TPD was carried out at 100–600 °C with a heating rate of 10 °C min⁻¹. The ammonia concentration in the effluent N₂ stream was monitored by a thermal conductivity detector (TCD).

2.4. Catalytic performance evaluation

The catalytic pyrolysis of waste tires was carried out in a micro-reactor system under atmospheric pressure. A precisely weighed amount of waste tires (1.00 g) and catalyst (0.50 g) were mixed intensively and loaded in a stainless steel tube, which was then put into the batch reactor. The reactor was heated with an electrical furnace. The temperature was measured and controlled by a thermocouple, with a heating rate of 10 °C min⁻¹ and a nitrogen flow of 30 mL min⁻¹.

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