



LPG catalytic cracking over the modified ZSM-5 by activated carbon and carbon nanotube templates: Synthesis, morphology and performance of catalysts



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ABSTRACT

Porous-structured, meso-microporous ZSM-5 zeolite (MZSM5) materials synthesized via in-situ blending of the reaction mixture $40\text{SiO}_2:\text{Al}_2\text{O}_3:4.5\text{Na}_2\text{O}:1500\text{H}_2\text{O}$ and carbon-nanotube or activated-carbon powder at certain established conditions were implemented into LPG catalytic cracking. The synthesized catalysts were characterized by X-ray powder diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), nitrogen adsorption–desorption isotherms, and temperature-programmed desorption of ammonia ($\text{NH}_3\text{-TPD}$). The impact of type and amount of carbon particles was investigated on properties such as morphology, crystallinity percentage, and the size of synthesized MZSM5 crystals. XRD and SEM measurements revealed that higher amorphous phase was found in MZSM5 synthesized by activated carbon. Applying the activated carbon into carbon nanotubes creates a lot of empty space between the particles in the crystal phase, which is inaccessible with regards to the BET results (not inside the crystal in order to access the active sites). However, the carbon nanotubes create corridor routes to the center of the crystalline particles, providing constant surfaces entirely accessible to the active sites of the catalyst. The experiments of LPG catalytic cracking were implemented by a fixed-bed reactor over the synthesized catalysts. The maximum yield of ethylene plus propylene was found to be 46% over MZSM5 synthesized with 30 wt% carbon nanotube.

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1. Introduction

ZSM-5 zeolites are widely used in industries due to their distinctive properties such as acidity and stability (Chenga et al., 2008; Kalipcilar and Culfaz, 2007; Khatamian et al., 2010; Petushkov et al., 2011; Wei and Smirniotis, 2006; Xianliang and Zhengbao, 2011; Zhu et al., 2009). The pore size of the ZSM-5 zeolites is typically 0.51×0.56 nm, which is appropriate for vital industrially applicable molecules such as alkanes, alkenes, benzene, phenol, aniline, and their derivatives (Zhang et al., 2003).

In the catalytic cracking process, diffusion is a challenging issue for the products and substrates. On the other hand, coke formation at the start of reaction time may block the pores of zeolite. Therefore, the formation of ZSM-5 with mesoporous structure is well-suited to reduce the diffusion resistance of the pore and to improve the sites activity. Mesopores are formed in different ways,

such as thorough alkali treatment (Gao and Tang, 2010; Li et al., 2011; Yoo et al., 2012; Zhao et al., 2011), carbon templates (Cho and Ryoo, 2012; Wei and Smirniotis, 2006) and carbon nanotube templates (Schmidt et al., 2001; Tang et al., 2006). Alkali treatment is not preferable as it is a desilication process that destroys the catalyst structure. Carbon nanotube templates form manageable mesopores, which maintain the structure of the catalyst and therefore preferable.

The present paper reports the synthesis of mesopores along with micropores, by templates of activated carbon and carbon nanotube with different carbon content (0–50 wt%), have created hierarchical structures for ZSM-5 zeolite. This study presents a novel approach in which activated carbon powder or carbon nanotube blended in the reaction mixture develop the mesopores through ZSM-5 crystals during the hydrothermal synthesis of the ZSM-5. Mesopores size varies depending on the type of carbon templates. The particle size of activated carbon was $<74,000$ nm, while that of carbon nanotubes was 20–40 nm. The characteristics of ZSM-5 are the function of temperature and reaction time as well as the percentage of carbon template. The optimum temperature

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and reaction time were obtained for pure-ZSM-5 production. The synthesized ZSM-5 catalysts were applied to the production of light olefins through LPG catalytic cracking. The effect of the type and carbon template content on the physicochemical properties and catalytic activities of ZSM-5 were investigated in this study. The LPG catalytic cracking products were analyzed by gas chromatography (GC) and the physicochemical properties of synthesized catalysts were studied by X-ray diffraction (XRD), N_2 adsorption and desorption isotherms (BET), temperature-programmed desorption of ammonia (NH_3 -TPD), transmission electron microscopy (TEM) and scanning electron microscope (SEM) analyses.

2. Experimental

2.1. Materials

Ludox[®] silica solAS-30 colloidal silica, 30 wt% suspension in water (Sigma-Aldrich), aluminum hydroxide (Riedel-de Haën), sodium hydroxide (Panreac Quimica SAU), and deionized water were used in the synthesis of ZSM-5. Zeolite H-form was performed by ammonium nitrate (Sigma-Aldrich). Activated carbon and carbon nanotubes (Pars Carbon Black) were used as a carbonic template to produce mesopores in zeolite.

2.2. Synthesis of pure-ZSM-5

The molecular structure of zeolites is $aSiO_2:bAl_2O_3:cNa_2O:dH_2O$, in which the value of the parameters was substituted as $a = 40$, $b = 1$, $c = 4.5$, and $d = 1500$ to produce pure-ZSM-5 (Noack et al., 2009; Wang et al., 2005; Phiriyawirut et al., 2003; Coker et al., 2001; Mentzen et al., 2006). ZSM-5 was synthesized as follows: Solution A: 0.72 g sodium hydroxide and 0.312 g aluminum hydroxide were dissolved in 28.2 ml deionized water, Solution B: 16 g silica sol was diluted with 14.6 ml deionized water. Solution A was slowly added to Solution B under vigorous stirring. The formed gel was stirred for 45 min until perfectly homogeneous. Therefore, the mixture was transferred into a Teflon-lined, 500 ml stainless-steel autoclave. ZSM-5 synthesis and the crystallization growth were implemented at various temperatures (190–200 °C) and time (38–48 h). The products were filtered on a Buchner funnel under vacuum, washed with deionized water, and then dried at 110 °C for 5 h. Calcination of the synthesized zeolite was avoided due to the use of inorganic template (TPA) (Hosseini et al., 2012; Karimi et al., 2012; Kumara et al., 2002; Petushkov et al., 2011; Xue et al., 2012; Zhu et al., 2009).

2.3. Synthesis of mesoporous ZSM-5

The gel mixture prepared in section 2.2 was mixed with activated carbon in different weight ratio of SiO_2 in silica sol (10, 20, 30, 40, and 50 wt%). The mixture was stirred for 30 min to obtain fully dispersed carbon particles. Then, the mixture was transferred into an autoclave to perform hydrothermal reactions under conditions in accordance with the provisions of section 2.2. After drying, the catalysts were calcined in a furnace at 600 °C for 5 h to remove the activated carbon deposited among the ZSM-5 crystals in order to create mesopores. The final ZSM-5 zeolites obtained were labeled as ZSM-5C(X), in which "X" is the weight percent of activated carbon. For example, 10 wt% of activated carbon was donated as ZSM-5C(10). In case of no carbon, the values of "X" is zero. The synthesized Na-form of ZSM-5 zeolites were converted into H-form ZSM-5 via three-times ion-exchanged treatment in 100 ml of 1 M NH_4NO_3 solution at 80 °C for 3 h, filtered, washed with deionized water, dried at 110 °C for 12 h, and finally, after three times of treatments, calcined in a furnace at 550 °C for 5 h. All procedures for carbon

nanotubes were similar to that for activated carbon, except that the stirring time of the synthesized gel and the calcination time of removing carbon nanotubes were 3 and 12 h, respectively. The reason for such longtime duration is the higher thermal resistance of carbon nanotubes. The catalysts obtained by carbon nanotubes were contributed as ZSM-5 CNT(X), where "X" is the weight percent of the nanotubes.

2.4. Characterization

The nature of the synthesized catalysts was characterized by XRD using $Cu-K\alpha$ radiation (40 kV, 40 mA, $\lambda = 1.78897 \text{ \AA}$) in the 2θ range of 5° – 50° , with a step size of 0.02. For SEM imaging, the powdered sample was dispersed on a carbon tape support with metal coating and was analyzed under the Hitachi S-4800 SEM with a field-emission gun. FESEM images were obtained under FESEM XL-30 (Zeiss, Oberkochen, Germany) with an accelerating voltage of 10 kV. TEM was carried out in a JEOL 1011 microscope operated at 100 kV. Samples were suspended in methanol and supported on a carbon-coated copper grid. Nitrogen adsorption–desorption isotherms were measured at 77 K by using the Quantachrome Instruments Autosorb-1 System. Prior to the adsorption measurements, the samples were degassed for 15 h at 393 K. The Brunauer–Emmett–Teller (BET) method was applied to estimate the specific surface areas. The micropore volume was calculated by a t-plot and the mesopore volume by subtracting the micropore volume from the total pore volume measured at a $P/P_0 = 0.984$. The pore size distribution was calculated from the adsorption branch of N_2 isotherm by using the Barrett–Joyner–Halenda (BJH) method. The NH_3 -TPD was measured by using a mass spectrometer (M-200GA-DM; Canon Anelva) as a detector of the quantity of desorbed ammonia. In all experiments, 50 mg of the sample was degassed at 300 °C for 1 h in flowing He and then cooled to 150 °C. At 150 °C, NH_3 was adsorbed on the sample by injecting pulses of 2 μ l/pulse. After NH_3 adsorption was saturated, the sample was flushed at 150 °C for 1 h with He to remove the excess NH_3 , the temperature was then programmed at 30 °C/min up to 700 °C in flowing He at 30 ml/min.

2.5. Catalytic tests

About 0.12 g of synthesized catalyst diluted with 0.6 g of silica was inserted in the reactor between quartz wool. The catalyst in the reactor was pre-treated by passing 40 ml/min of air for 1 h, followed by 25 ml/min of nitrogen for 1 h at 650 °C. LPG at the rate of 27 ml/min (propane: 48%, n-butane and iso-butane: 52%) diluted in N_2 as a carrier gas entered into an atmospheric, fixed-bed quartz reactor with the length and diameter of 60 and 1 cm, respectively, and passed over the synthesized HZSM-5, where the temperature was controlled at 650 °C. The products obtained were analyzed by on-line Agilent refinery gas analyzer with a capillary aluminum column (100 m \times 0.50 mm), a flame ionization detector (FID), and two thermal conductivity detectors (TCD).

3. Results and discussion

3.1. Effect of reaction time and temperature on ZSM-5 synthesis

In order to optimize the reaction conditions, the synthesis of pure-ZSM-5 zeolite was conducted at 192 °C and at time intervals of 38, 40, 42, 44, 46, and 48 h. In Fig. 1a, the XRD patterns are shown for the reaction performed at 192 °C over a reaction time of 38–48 h. Here, the peaks are shown in the 2θ ranges of 7 – 9° and

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