Coking behaviors and kinetics on HZSM-5/SAPO-34 catalysts for conversion of ethanol to propylene

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ABSTRACT

The coke deposition on HZSM-5/SAPO-34 composite catalysts has been studied in the conversion of ethanol to propylene. The HZSM-5/SAPO-34 composite catalysts were synthesized by hydrothermal method (ZS-HS) and fully blending (ZS-MM). The used catalysts were characterized by XRD, N_2 adsorption–desorption, TGA, TPO, elemental analysis, FTIR and XPS. The coking kinetics on both ZS-HS and ZS-MM has been investigated and their coking rate equations were obtained. The used ZS-MM catalyst had higher amount of coke and lower $n_C:n_H$ than the used ZS-HS. 90% of the coke was deposited in the micropores of ZS-HS, while almost 45% of the coke located in the micropores of ZS-MM. The coke deposited on ZS-HS catalyst was mainly graphite-like carbon species, whereas dehydrogenated coke species was the major on ZS-MM. The coking activation energy of ZS-MM was lower than that of ZS-HS, and the coking rate on ZS-MM was faster than on ZS-HS. In addition, the regeneration of ZS-MM catalyst showed that it had a good hydrothermal stability. The differences on coking behaviors on the two catalysts were due to their different acidic properties and textures.

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1. Introduction

In recent years, much attention has been focused on the production of propylene, which is important raw chemical for producing polymers. However, propylene production was in short supply, due to the growing demand for its downstream products. The catalytic conversion of ethanol into propylene has got wide attention. It is considered to be a carbon-neutral process using renewable biomass. In addition, ethanol conversion to hydrocarbons can reduce damage to the environment and relieve the shortage of oil [1].

Ethanol conversion includes some side reactions, which lead to the formation of coke on catalysts. Coke can block channels and poison acid sites. Thus, coke behavior changes the distribution of products, reduces the activity or even deactivates the catalysts [2]. Phung et al. [3] and Madeira et al. [4] found that the different coking behaviors of zeolite catalysts for ethanol conversion were closely related to confinement effects on different zeolite cavities. In addition, it was found that the stream treatment created new mesopores which could accommodate a part of coke and suppress coke formation in micropores [5]. Ramasamy et al. [6] reported that a large amount of mesoporous in nano sized

hierarchical HZSM-5 contributed to shorter diffusion path length, faster removal the coke precursors in channels and enhanced the anti-coking ability of catalyst. On the other hand, Madeira et al. [7] reported that the amount of B acid sites played important roles in both products distribution and coke formation. Sheng et al. [5] found that the modification of catalysts acidity significantly changed the products in ethanol conversion. However, until now few literatures on coke behavior and kinetics on the catalysts for ethanol to propylene have been published. Coking deactivation was a significantly barrier for real application of the catalyst.

In our previous work [8,9], HZSM-5/SAPO-34 binary structure composite catalysts were prepared by different methods and used for conversion of ethanol to propylene. The HZSM-5/SAPO-34 catalyst prepared by fully blending showed the highest propylene yield of 34.5 wt% in isothermal fixed-bed reactor under the proper reaction conditions than other reported catalysts.

Hence, in this work, the used HZSM-5/SAPO-34 catalysts were characterized by X-ray diffraction (XRD), N_2 adsorption–desorption, thermal gravity analysis (TGA), temperature-programmed oxidation (TPO), elemental analysis, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Based on the obtained results, the coking kinetics of the catalysts was studied. The location and composition of coke on the used catalysts were investigated in detail. In addition, the influences of acidic and textural properties of the catalysts on the coking behavior were discussed.

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2. Experimental

2.1. Catalyst preparation

HZSM-5/SAPO-34 composite catalysts were synthesized by hydrothermal method [8,9]. Firstly, 10 g of pseudoboehmite (AlOOH, Xibei Chem.) was added to 98 g of tetramethylammonium hydroxide (TEAOH, 25 wt% in water, Aladdin Chem.) and stirred for 30 min. Secondly, 16 g of orthophosphoric acid (85 wt%, Ruijing Chem.) and 6 g of silica sol ($SiO_2 = 30$ wt%, Xianshiji Chem.) were added dropwise and stirred to obtain white homogeneous slurry. Then, a certain amount of HZSM-5 powder (Nankai Unv., $SiO_2/Al_2O_3 = 25$) was added. The final mixture was aged overnight and transferred into a Teflon-lined stainless steel autoclave. The crystallization was done at 200 °C for 72 h. The resultant solid product was separated by filtration, washed several times, dried at 110 °C overnight and calcined in air at 550 °C for 7 h. The sample was named ZS-HS.

For comparison, HZSM-5/SAPO-34 catalyst was prepared by fully blending of HZSM-5 (Nankai Unv., $SiO_2/Al_2O_3 = 25$) and SAPO-34, which was named ZS-MM. SAPO-34 was prepared as similar as the preparation of ZS-HS, except the addition of HZSM-5. The weight fraction of SAPO-34 in the ZS-HS and the ZS-MM was estimated from a plot of XRD peak intensity of SAPO-34 ($2\theta = 20.6°$) versus weight fraction of SAPO-34. The plot could be obtained by correlating the relationship of XRD peak intensity of SAPO-34 ($2\theta = 20.6°$) with the known SAPO-34 weight fraction in HZSM-5/SAPO-34 mixture prepared by mechanical blending method. Table 1 shows the texture and acidity of these prepared catalysts, HZSM-5 and SAPO-34 [8,9].

2.2. Catalyst test

The conversion of ethanol was carried out in a continuous-flow fixed-bed reactor. The reactor, made of stainless steel, had an internal diameter of 10 mm and a length of 650 mm. The space up and down the catalyst bed in the reactor was filled with quartz wool. The weight of the catalyst bed was ca. 10 mg and the size of the catalyst particles were ca. 20–40 mesh. The reaction temperature was controlled by a temperature controller (YUDIAN AI-518/518P) and measured by a K-type thermal couple. Two additional temperature controllers were used: one was to monitor the temperature distribution of the reactor, and the other was to control the transfer line temperature from the reactor outlet to the gas chromatography. Ethanol (Beijing Chem. Co., A.R.) was injected into a preheater by a syringe pump (Lab Alliance series III) and mixed with N_2. The gaseous mixture passed through the catalyst bed. The off-gas was kept at 120 °C by heating belt. A small fraction of outlet gas made up of unreacted reactant and products was analyzed by gas chromatography (Ruimin Anal. GC-2060) with two analytical modules. CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8, C_4H_{10} and C_5^+ (aliphatic and aromatic hydrocarbons) were separated by a KB-Al_2O_3/Na_2SO_4 capillary column (50 m × 0.32 mm × 15 μm) and detected by a flame ionization detector (FID). Ethanol was identified by a GDX-103 packed column and detected by a thermal conductivity detector (TCD). The conversion of ethanol and the yield of products were respectively calculated by the following formula.

Conversion of ethanol (wt%)

$$= (\text{ethanol}_{\text{in feed}} - \text{ethanol}_{\text{in off-gas}}) \times 100\%/\text{ethanol}_{\text{in feed}} \quad (1)$$

$$\text{Selectivity}_i \text{ (wt\%)} = A_i \times n_i \times 100\% / \left(\sum A_i \times n_i\right) \quad (2)$$

$$\text{Yield}_i \text{ (wt\%)} = \text{Conversion of ethanol} \times \text{selectivity}_i \times 100\% \quad (3)$$

where A represents the peak area, and n represents the number of carbon atoms in the product i.

The coke deposition measurement was performed on a thermogravimetric analyzer (Mettler TGA/SDTA851^e) under airflow (50 mL/min) with a heating rate of 10 °C/min from 50 to 700 °C. The coke amount of the used catalyst was calculated as follows:

$$C(\text{wt\%}) = (m_{\text{used catalyst}} - m_{\text{fresh catalyst}}) \times 100\% / m_{\text{used catalyst}} \quad (4)$$

Here, $m_{\text{fresh catalyst}}$ and $m_{\text{used catalyst}}$ denote the mass of fresh catalyst and the mass of used catalyst, respectively.

2.3. Catalyst characterization

The used catalysts were characterized by XRD, N_2 adsorption–desorption, FTIR and XPS. Powder X-ray diffraction patterns were obtained by RogakuRotflex D/Max-C power X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15046$ nm) operated at 40 kV and 30 mA. N_2 adsorption–desorption characterization of the samples was performed at -196 °C by Micromeritics ASAP400 instrument. Prior to the adsorption, samples were outgassed in N_2 flow at 200 °C for 3 h. Specific surface area was calculated according to BET method. Micropore volume was obtained by t-plot analysis of the adsorption isotherm. Mesopore volume was obtained by BJH method. The TPO experiment was made in a continuous flow fixed-bed reactor system with thermal conductivity detector (TCD, BeifenRuili GC-3400). NH_3-TPD was carried out in 30 mL/min air flow and heated at a rate of 10 °C/min from 50 to 600 °C. The elemental analysis was performed by Elementarvario Macro instrument. FTIR spectra of these samples were recorded by Nicolet FTIR 6700 spectrometer with the resolution of 4 cm^{-1}. XPS spectra were performed by Thermo AXIS Ultra DLD instrument with an excitation source of Al $K\alpha$ radiation (1486.7 eV, 15 kV).

2.4. Coking kinetics

The coking kinetics on HZSM-5/SAPO-34 catalysts in ethanol transformation was studied by a thermal gravity analyzer (TGA). For study of coking kinetics, the catalyst was collected after 6 h of time on stream (TOS) under different reaction conditions. The average coking rate (dc/dt) was identified as the coke amount deposited on unit mass of catalyst in unit time. The coking rate equation is expressed as follows [10]:

$$dc/dt = kp^n \quad (5)$$

Here, dc/dt is the coking rate, k is the rate constant, p is the ethanol partial pressure, and n is the reaction order.

The reaction rate constant can be expressed based on Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad (6)$$

Eq. (3) is obtained by combining Eqs. (5) and (6):

$$dc/dt = Ae^{-E_a/RT} p^n \quad (7)$$

The logarithm form of Eq. (7) is:

$$\ln(dc/dt) = \ln A + n\ln p - E/RT \quad (8)$$

The pre-exponential factor A, the reaction order n, the coking activation energy E_a and the reaction rate constant k can be obtained by linear fitting of $\ln(dc/dt)$ versus $\ln p$ and $\ln(dc/dt)$ versus $1/T$.

3. Results

3.1. Coking kinetics of ZS-MM and ZS-HS catalysts

The effect of reaction temperature on coking behaviors of HZSM-5/SAPO-34 composite catalysts in ethanol conversion was