The fabrication of TiO$_2$-supported zeolite with core/shell heterostructure for ethanol dehydration to ethylene

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**Abstract**

The TiO$_2$-supported zeolite with core/shell heterostructure was fabricated by coating aluminosilicate zeolite (ASZ) on the TiO$_2$ inoculating seed via in situ hydrothermal synthesis. The catalysts were characterized by transmission electron microscope (TEM), X-ray diffraction (XRD), nitrogen physisorption (BET), and Fourier transform infrared spectroscopy (FT-IR). The surface acidity of the catalysts was measured by pyridine-TPD method. The catalytic performance of the catalysts for ethanol dehydration to ethylene was also investigated. The results show that the TiO$_2$-supported zeolite composite catalyst with core/shell heterostructure exhibits prominent conversion efficiency for ethanol dehydration to ethylene.

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1. Introduction

Ethylene, which is conventionally produced from the non-renewable petroleum resources, is one of the major feedstocks in the petrochemical industry. At present, with the heavy dependence on petroleum for energy supply and depleting of oil reserves, biomass utilization has been drawing increasing attention by many countries. It is becoming a potential and alternative route to meet the demand of ethylene with a complementary supply from a renewable and environmental friendly feedstock, bio-ethanol.

The catalyst plays a crucial role in the process of ethanol dehydration to ethylene. Nowadays, the widely used catalyst in industrial application is still $\gamma$-Al$_2$O$_3$ [1–3], and other catalysts have also been developed such as zeolite [4], silica-alumina [5], heteropolyacid [6–9], and transition metal oxides [10–13]. Among them, zeolite has been proven to be a promising catalyst in improving the conversion efficiency of ethanol dehydration to ethylene, and lowering the operation temperature compared with $\gamma$-Al$_2$O$_3$ [14]. In order to further improve the catalytic performance of ethanol dehydration, there are numerous work on the modification of catalysts have to be done. For example, ZSM-5 exchanging with metal ions such as cobalt, manganese, zinc, and strontium was reported to be more active than $\gamma$-Al$_2$O$_3$ [15].

The TiO$_2$/ZSM-5 composite catalyst was also found to be an effective promoter in enhancing the performance of ethanol dehydration. For example, TiO$_2$/ZSM-5 [20] catalyst has been found to be much more active than $\gamma$-Al$_2$O$_3$. Our reported results previously also showed that TiO$_2$/zeolite 4A composite catalyst exhibits much better dehydration performance than the original zeolite 4A [21].

In this work, we report the synthesis of the TiO$_2$-supported zeolite composite catalyst with core/shell heterostructure via in situ hydrothermal method, and investigate the catalytic performance for ethanol dehydration to ethylene.

2. Experimental

2.1. Catalyst preparation

The TiO$_2$-supported zeolite composite catalyst with core/shell heterostructure was fabricated by coating ASZ on the TiO$_2$ inoculating seed via in situ hydrothermal synthesis [22,23]. First, a starting sol mixture was prepared as follow: we used 32.14 g of aluminium chloride as the Al source, 72 ml of ethyl silicate as the Si source, 40 ml of 0.2 M NaOH as the alkali source and 3 g of cetyltrimethyl ammonium bromide (purity $>$99.9%) as the template reagent, and they were dissolved in 230 ml of distilled water. The obtained mixture was put into a Teflon-lined stainless steel autoclave (500 ml), and then it was hydrothermally treated with continuous stirring for 36 h at 150 °C. After separated with filtration and washed with distilled water, the resultant product was...
dried at 80 °C for 6 h in the oven and then calcined in a muffle at 600 °C for 4 h.

2.2. Catalyst characterization

Transmission electron microscope (TEM) were carried out by using a JEM-1010 microscope with an acceleration voltage of 100 kV. The phase identification of the catalysts was performed by X-ray diffraction (XRD, X’ PERT-PRO, PANALYTICAL Incorporated, Holland) equipped with Cu Kα radiation with an accelerating voltage of 40 kV and current of 40 mA. The patterns were recorded over the 2θ angle ranging from 5° to 70° at a scanning rate of 1.5°/min. Specific surface area, pore volume and pore diameter of the samples were measured by nitrogen adsorption–desorption technique using an ASAP 2020 instrument (Micromeritics Instrument Corporation, USA). The pore volume and pore diameter were estimated by the BJH (Barrett–Joyner–Halenda) method, and the surface area (SBET) was calculated by Brunauer–Emmett–Teller (BET) method. The FT-IR spectra of the samples were recorded in the form of KBr pellets in region of 4400–400 cm⁻¹ on a FTS 3000 Fourier transform infrared (FT-IR) spectrometer (Varian, USA). The pyridine-TPD was measured by a thermogravimetric analyzer (TG, STA409C/PC, NETZSCH Incorporated, Germany) at a heating rate of 10 °C/min in the presence of dry N₂ (30 ml/min). Before detection, the samples were firstly preheated at 110 °C for 2 h, and then they were kept in a desiccator accompanied with an open beaker containing enough pyridine liquid for 6 days at room temperature. Then the pyridine-TPD was measured with approximately 10 mg sample from 40 to 800 °C.

2.3. Dehydration performance measurement

The measurement of dehydration performance for catalysts was carried out in a stainless steel-made, tubular, continuous flow fixed-bed reactor (inner diameter 9 mm and length 300 mm) under atmospheric pressure. 4.0 g of catalyst was loaded in the identical temperature zone of the reactor. After the reactor was purged by nitrogen flow, the weight hourly space velocity (WHSV) is kept at 1.8 h⁻¹. Absolute ethanol was injected by a pulse micro-liquid pump to a vaporizer and subsequently passed into the reactor with the operation temperature range from 210 to 420 °C. The temperatures of the vaporizer and the reactor were controlled by the thermocouples. The gas phase products were analyzed by another gas chromatograph (Agilent 6890) equipped with a TCD detector at an oven temperature of 90 °C with Ar as carrier gas. The liquid phase products were examined by another gas chromatograph (Agilent 6820) equipped with a FID detector in a temperature-programmed course from 40 to 100 °C with N₂ as carrier gas. The conversion of ethanol (Cethanol) is defined as the molar ratio of converted ethanol to the total injected ethanol. The selectivity of ethylene (Sethylene), the selectivity of diethyl ether (SDDE) and the selectivity of acetaldehyde (Schetalde) are defined as the molar ratio of ethylene, diethyl ether and acetaldehyde to the total converted ethanol, respectively.

3. Results and discussion

Fig. 1 shows TEM images of ASZ and the TiO₂-supported zeolite composite catalyst after calcination at 600 °C. It can be seen from Fig. 1a that ASZ sample has uniform particle size of about 50 nm, and the particles are roughly spherical. From Fig. 1b, the core–shell structure for TiO₂-supported zeolite particles can be clearly seen, it is due to the difference in electron penetrability between the TiO₂ core and the aluminosilicate zeolite shell.

XRD patterns of calcined ASZ, TiO₂, and TiO₂-supported zeolite samples are shown in Fig. 2. ASZ exhibits only one broad diffraction peak at 2θ value of about 23°, suggesting an amorphous aluminosilicate zeolite rather than a crystalline zeolite [24,25]. The TiO₂-supported zeolite sample also reveals characteristic peaks of the crystal phase of TiO₂ in anatase besides the diffraction peak of amorphous ASZ, indicating that the crystal phase of TiO₂ inoculating seed has not changed during the process of hydrothermal synthesis.

The FT-IR spectra are collected in order to verify the formation of the framework structure of ASZ for the synthesized samples. As shown in Fig. 3, IR results confirm the formation of ASZ showing distinct absorbance bands near 3500 cm⁻¹ (–OH stretching), 1630 cm⁻¹ (the peak of water), 1100 cm⁻¹ (asymmetric vibrations of Si–O–Si and Si–O–Al), 560 cm⁻¹ (TiO₂ in anatase and five-membered rings) [26]. The FT-IR spectra of TiO₂-supported zeolite composite catalyst with core/shell heterostructure are similar to that of ASZ.

Fig. 1. TEM images of (a) ASZ and (b) TiO₂-supported zeolite.

Fig. 2. XRD pattern of calcined ASZ, TiO₂, and TiO₂-supported zeolite catalysts.
As listed in Table 1, the specific surface areas ($A_{\text{BET}}$) and the pore volume ($V_P$) of TiO$_2$, ASZ, and TiO$_2$-supported zeolite composite catalyst are 4.1952 m$^2$/g and 0.019 cm$^3$/g, 602.92 m$^2$/g and 0.58 cm$^3$/g, and 542.51 m$^2$/g and 0.39 cm$^3$/g, respectively. It can be found that the specific surface area and the pore volume of TiO$_2$ are relatively small. The specific surface area and the pore volume of the TiO$_2$-supported zeolite composite catalyst with core/shell heterostructure have a little decrease compared with that of ASZ. It is likely due to ASZ coating on low-surface-area TiO$_2$.

Pyridine-TPD measurement was carried out to study the acidic properties of ASZ and TiO$_2$-supported zeolite composite catalyst. From a qualitative point of view [27], the peaks with desorption temperature below 200°C, between 200 and 400°C and higher than 400°C are corresponding to the weak acid sites, moderate acid sites and strong acid sites, respectively. As shown in Fig. 4, the weak acidity of TiO$_2$-supported zeolite composite catalyst is similar to that of ASZ, and the strong acid sites, specially the relative intensity of moderate acid sites become much higher. The number of moderate acid sites is commonly recognized to be responsible for catalytic dehydration of ethanol to ethylene [28,29]. So the variation of moderate acidity between TiO$_2$-supported zeolite composite catalyst and ASZ should be paid more attention. The peaks of moderate acid site on the TiO$_2$-supported zeolite composite catalyst are much more in evidence compared with that of ASZ. The peak for the ASZ between 200 and 400°C seems like overlapping of two peaks, and the peaks for TiO$_2$-supported zeolite composite catalyst split distinctly.

![FT-IR spectra of ASZ and TiO$_2$-supported zeolite catalysts.](image1)

**Fig. 3.** FT-IR spectra of ASZ and TiO$_2$-supported zeolite catalysts.

As listed in Table 1, the specific surface areas ($A_{\text{BET}}$) and the pore volume ($V_P$) of TiO$_2$, ASZ, and TiO$_2$-supported zeolite composite catalyst are 4.1952 m$^2$/g and 0.019 cm$^3$/g, 602.92 m$^2$/g and 0.58 cm$^3$/g, and 542.51 m$^2$/g and 0.39 cm$^3$/g, respectively. It can be found that the specific surface area and the pore volume of TiO$_2$ are relatively small. The specific surface area and the pore volume of the TiO$_2$-supported zeolite composite catalyst with core/shell heterostructure have a little decrease compared with that of ASZ. It is likely due to ASZ coating on low-surface-area TiO$_2$.

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| Sample                | $A_{\text{BET}}$ (m$^2$/g) | $V_P$ (cm$^3$/g) |
|-----------------------|-----------------------------|------------------|
| TiO$_2$               | 4.1952                      | 0.019            |
| ASZ                   | 602.92                      | 0.58             |
| TiO$_2$-supported zeolite | 542.51                      | 0.39             |

**Table 1**

Specific surface area and pore structure of TiO$_2$, ASZ, and TiO$_2$-supported zeolite.

![Pyridine-TPD profiles of calcined ASZ and TiO$_2$-supported zeolite catalysts.](image2)

**Fig. 4.** Pyridine-TPD profiles of calcined ASZ and TiO$_2$-supported zeolite catalysts.

![Pyridine-TPD profiles of calcined ASZ and TiO$_2$-supported zeolite catalysts.](image3)

**Fig. 5.** Effect of reaction temperature on (a) the conversion of ethanol and the selectivity of ethylene; (b) the selectivities of diethyl ether and acetaldehyde; (c) the formation rate of ethylene over the studied catalysts.
Fig. 5 shows the conversion of ethanol, the selectivities of ethylene, diethyl ether and acetaldehyde as well as the formation rate of ethylene as a function of reaction temperature over TiO$_2$, ASZ, and TiO$_2$-supported zeolite composite catalyst, respectively. The reaction of ethanol dehydration to ethylene over TiO$_2$-supported zeolite composite catalyst starts at 210$^\circ$C, while that over ASZ or TiO$_2$ does at 240$^\circ$C. The conversion of ethanol and the selectivity of ethylene increase with the rising of the reaction temperature, on the contrary, the selectivities of diethyl ether and acetaldehyde decrease. The formation rate of ethylene over the TiO$_2$-supported zeolite composite catalyst was eight times higher than that over ASZ or TiO$_2$ at 420$^\circ$C. It is obvious that the TiO$_2$-supported zeolite composite catalyst can remarkably improve the performance of ethanol dehydration to ethylene, and it at the same time restrains the formation of byproducts such as diethyl ether and acetaldehyde under the same reaction condition.

As for the mechanism of ethanol dehydration, Hassan [30] suggested that ethanol firstly adsorbs on the acid center of the catalyst surface and then forms an oxonium ion C$_2$H$_5$OH$^+$, which either reacts with another C$_2$H$_5$OH molecule to form the foremost product of diethyl ether or reacts with dehydrates to form the ethylene. The moderate acid site on the surface of the catalyst has an important influence on the catalytic dehydration performance of ethanol [25]. TiO$_2$ is usually used as an anode-supported material. For example, it is used in Dye Sensitized Cell (DSC) to receive the electrons from the excited dye sensitizer and then transfer them to the cathode. For TiO$_2$-supported zeolite composite catalyst, TiO$_2$ would receive the electrons from the ASZ, and thus result in increasing number of effective acid sites determined by pyridine-TPD, as shown in Fig. 4. Therefore, the TiO$_2$-supported zeolite composite catalyst exhibits much higher catalytic efficiency for ethanol dehydration to ethylene than ASZ or TiO$_2$ does.

4. Conclusion

The TiO$_2$–supported zeolite composite catalyst with core/shell heterostructure was fabricated by coating ASZ on the TiO$_2$ inoculating seed via in situ hydrothermal synthesis. As a result of anatase TiO$_2$ functions as an acceptor of electrons, as an anode-supported material. For example, Dye Sensitized Cell (DSC) to receive the electrons from the excited dye sensitizer and then transfer them to the cathode. For TiO$_2$-supported zeolite composite catalyst, TiO$_2$ would receive the electrons from the ASZ, and thus result in increasing number of effective acid sites determined by pyridine-TPD, as shown in Fig. 4. Therefore, the TiO$_2$-supported zeolite composite catalyst exhibits much higher catalytic efficiency for ethanol dehydration to ethylene than ASZ or TiO$_2$ does.

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