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Dehydration reaction of bio-ethanol to ethylene over modified SAPO catalysts

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Mn modified SAPO-11 (Mn-SAPO-11), Zn-SAPO-11, Mn-SAPO-34 and Zn-SAPO-34 were first synthesized with hydrothermal method in the laboratory. Dehydration of ethanol to ethylene over SAPO-11, SAPO-34 and four materials above as catalysts was carried out and Mn-SAPO-34 exhibited the best conversion and selectivity (99.35% and 98.44%, respectively) at 340 °C. The introduction of Mn^{2+} or Zn^{2+} into the SAPO channel generated in Mn-SAPO or Zn-SAPO samples was proved by X-ray diffraction (XRD), scanning electron microscopy (SEM) and nitrogen adsorption. NH_3-TPD study revealed that modification of Mn^{2+} or Zn^{2+} in the SAPO framework led to increase the weak acid strength and give rise to weak acid sites. The effects of operation parameters, such as loading amount, modification methods, reaction time, reaction temperature, mass space velocity and concentration of ethanol have also been investigated experimentally.

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1. Introduction

Ethylene is one kind of important material for petrochemical industry and is mainly derived from thermal cracking of petroleum or nature gas feedstock. The cracking process requires high temperature of 600–1000 °C. In recent years, with the shortage of natural resource and energy, and also with the soaring prices of crude oil, the way of bio-ethanol catalytic dehydration to ethylene has been paid more and more attention compared with the traditional route because of some advantages, such as the reduction of CO_2 emission [1,2], low production cost and energy consumption.

Two competitive ways occur during ethanol dehydration [3]:

$$C_2H_5OH \rightarrow C_2H_4 + H_2O + 44.9\ \text{kJ/mol} \quad (1)$$

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O - 25.1\ \text{kJ/mol} \quad (2)$$

The first reaction (main reaction, intra-molecular dehydration of ethanol to ethylene) is endothermic while the second one (side reaction, inter-molecular dehydration of ethanol to diethyl-ether) is exothermic. Diethyl-ether is produced in significant quantities at low temperature; however, high temperatures favor intra-molecular dehydration. Therefore, it was a critical issue to find catalyst with high catalytic activity for ethylene at relatively low temperature [4].

Bio-ethanol obtains based on biomass as raw material through fermentation and always contains amount of water. The concentration of ethanol is usually low, only about 10%. And there are many other impurities in the fermentation process. As a result, a lot of energy is consumed in the process of separation and purification through distillation. Ethylene would be obtained through one-step catalytic low concentrations ethanol dehydration at atmospheric pressure if the right catalyst was chosen. This process has many advantages, such as low energy consumption, simple equipment, and easy to control.

Many solid acid catalysts have been employed for the dehydration of ethanol [5–11]. With earlier γ-alumina (Al_2O_3) catalyst, ethanol dehydration required higher reaction temperature (400–450 °C) and offered lower ethylene yield (80%) [12,13]. The obvious disadvantage was a purification process of bio-ethanol with high energy consumption usually needed because of the poor catalytic properties when bio-ethanol solution contained large amount of water as reactant over Al_2O_3 catalyst was used. HZSM-5 zeolite was focused recently and a ethanol conversion of 98% at lower temperature (300 °C) was reported with it [10,14]. However, the strong acidity and unequally distribution of acid sites in HZSM-5 would lead to the by-production of C_4, so the catalyst easily occurred on coking deactivation [15].

In 1984, Lok et al. [16] introduced Si into $AlPO_4$ to synthesize new family of silicoaluminophosphate materials SAPO-*n*. Due to its narrow pores, extending in three dimensions and mild acidity, SAPO was successfully applied in the MTO (methanol to olefins) process [17–19] and was believed to be a promising catalyst in terms of activity and selectivity to light olefins [20]. Arias et al. [21]

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reported the dehydration of ethanol over SAPO-11 catalyst. The yield of ethylene achieved about 90% at 320 °C. In order to improve the yield of ethylene, Zhang et al. [13] chose metal doped-SAPO as catalyst, the best yield of ethylene was 92.3% for dehydration of ethanol at 350 °C over Ni-substituted SAPO-34. Unfortunately, the yield only increased about 2% at the cost of improving temperature by 30 °C. So far dehydration reaction of bio-ethanol to ethylene has been studied extensively. Thus, a systematic study is necessary for investigating the influence of reaction conditions on the catalytic properties over modified SAPO.

In this work, we aimed at investigating a new catalyst capable of exhibiting high efficiency at lower temperature. SAPO-11 and SAPO-34 were modified by Mn^{2+} and Zn^{2+} with hydrothermal method and impregnation method, and then their activities were compared with SAPO-11, SAPO-34 in the dehydration of ethanol to ethylene. A systematic study of the influence of reaction conditions, such as loading amount, modification methods, reaction time, reaction temperature, mass space velocity and concentration of ethanol, on the catalytic properties have also been investigated. This work will build a foundation to industrial production of ethylene by bio-ethanol dehydration process with the economic value and strategic significance.

2. Experimental

2.1. Catalyst preparation

Commercial SAPO-11 and SAPO-34 were obtained from Fushun Catalyst Factory and Dalian Institute of Chemical Physics, respectively. The final composition was $(Si_{2.54}Al_{19.4}P_{18.1})O_{80}$ for SAPO-11 and $(Si_{5.68}Al_{33.48}P_{27.28})O_{130}$ for SAPO-34. Hydrothermal method is described as the following steps. SAPO powder was diluted in water and mixed well with zinc nitrate or manganese nitrate solution of different concentration at room temperature. The mixture was stirred for 2 h, and then transferred to stainless steel reactor with Teflon-lined to crystallization for 2 h at 150 °C. The product was filtrated, washed, and dried at 120 °C for 2 h, followed by calcining at 600 °C for 4 h. Impregnation method was almost the same as above without the crystallization step.

2.2. Catalyst characterization

X-ray diffraction (XRD) analysis was carried out in a Japan Science D/max-IIIA diffractometer in the scan range of 2θ between 5° and 90° using Cu Kα as source at 30 kV, 20 mA. The morphology of the samples was examined by scanning electron microscope (SEM) (S-360 from Cambridge University Cambridge Company) at 1.0 kV.

The acidity strength and its distribution were analyzed by NH_3 adsorption and NH_3-TPD using TP-5000 multi-function instrument adsorption (Tianjin Instrument Co., Ltd.). 0.1 g catalyst sample was heated at 150 °C, and then at this temperature for impulse NH_3 adsorption. When saturated adsorption was achieved, temperature was first decreased to 50 °C for 60 min, then programmed to increased to 800 °C under the heating up rate of 10 °C/min.

The specific surface areas and the pore distribution of the catalysts were determined by the nitrogen physisorption using the BET method in NOVA 4000 instruments (Quantachrome Instruments, USA).

2.3. Catalytic reaction

Experimental setup used for this study is presented in Fig. 1. Catalytic reaction studies were performed in a fixed bed micro-reactor (φ8 mm × 300 mm). Ethanol was changed through a micro pump. Usually the reaction charged 2 g of catalyst. The products were analyzed on gas chromatograph (Shimadzu GC-2010) with FID using Porapak-Q column at 160 °C.

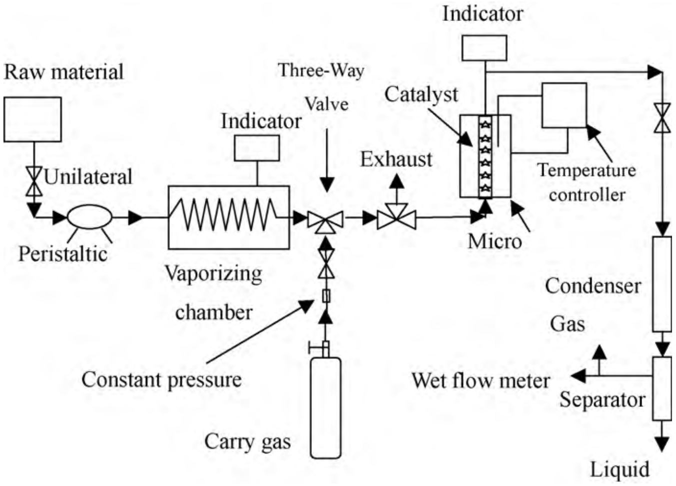

Fig. 1. Catalyst experimental setup.

2.4. Calculation

In this paper, the weight hourly space velocity (WHSV) is defined as the ratio of the hourly feed molar flow rate of ethanol and water mixture to the catalyst molar. The ethylene selectivity (S_{ethylene}), the diethyl-ether selectivity ($S_{\text{diethyl-ether}}$), the propylene selectivity ($S_{\text{propylene}}$), the ethanol conversion (C_{ethanol}) and the ethylene yield (Y_{ethylene}) are defined as the following:

$$S_{\text{ethylene}} = \left(\frac{m_{e1}}{m_{e0} - m_e}\right) \times 100\% \quad S_{\text{diethyl-ether}} = \left(\frac{m_{e2}}{m_{e0} - m_e}\right) \times 100\%$$

$$S_{\text{propylene}} = \left(\frac{m_{e3}}{m_{e0} - m_e}\right) \times 100\% \quad C_{\text{ethanol}} = \left(\frac{m_{e0} - m_e}{m_{e0}}\right) \times 100\%$$

$$Y_{\text{ethylene}} = \left(\frac{m_e}{m_0}\right) \times 100\%$$

Hereinto m_{e1}, m_{e0}, m_e, m_{e2}, m_{e3}, m_e, m_0 are defined as the amount of ethanol convert into ethylene, the amount of ethanol before reaction, and the amount of ethanol after reaction, the amount of ethanol convert into diethyl-ether, the amount of ethanol convert into propylene, the amount of ethanol in fact, the amount of ethanol in theory, respectively.

3. Results and discussion

3.1. Catalytic performance of modified SAPO-11 and SAPO-34

SAPO-11 and SAPO-34 were commercial catalysts. Mn-SAPO-11, Zn-SAPO-11, Mn-SAPO-34 and Zn-SAPO-34 were obtained through hydrothermal method with the same metal loading amount. Catalytic testing of ethanol was carried out over these catalysts. The results are illustrated in Fig. 2.

The catalytic performance of SAPO-11 exhibited excellent. When modified with Mn^{2+} or Zn^{2+}, the catalytic activity decreased according to the lower ethylene selectivity (76.7% and 69.9%) and ethanol conversion (92.2% and 86.9%) and the higher diethyl-ether selectivity (15.1% and 16.9%). This result showed that the incorporation of Mn^{2+} or Zn^{2+} into SAPO-11 surface was unfavorable to catalytic activity. In contrast, Mn^{2+} or Zn^{2+} modified SAPO-34 presented noticeable better catalytic activity than SAPO-34. Moreover, SAPO modified with Mn^{2+} showed higher efficiency than modified with Zn^{2+}. In summary, conversion of ethanol and selectivity of ethylene decreased in the following order Mn-SAPO-

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