Enhanced ethylene selectivity and stability of Mo/ZSM5 upon modification with phosphorus in ethane dehydrogenation

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ABSTRACT

Nonoxidative conversion of ethane to ethylene and/or BTX (benzene, toluene, and xylene) suffers rapid deactivation due to coke deposition. We report here the effects of phosphorus modification on the stability and activity of Mo/ZSM5 for nonoxidative conversion of ethane. The results show that the ethylene and BTX yield and stability are significantly enhanced upon modification with 2.5 wt.% P. NH_3 TPD, pyridine FTIR, ^{1}H MAS NMR, ^{27}Al MAS NMR, ^{31}P MAS NMR, [129]Xe NMR, XPS, UV–visible diffuse reflectance spectra (UV–vis DRS), and nitrogen physisorption were carried out to understand the effects of P on the structure of Mo/ZSM5 and its correlation with catalytic performance. The presence of P reduces the acid strength and density, changes the channel system of ZSM5 by forming thermally stable SAPO-like interfaces with the framework Al, and improves the dispersion of molybdenum. Rapid deactivation still occurs on Mo/ZSM5 with 1 wt.% P due to the existence of denser silanol groups, more isolated Mo species, and reduced aperture size with little change in effective micropore volume. A higher P loading (2.5 wt.%) leads to less dense silanol groups and less reduced but stable molybdenum species, and simultaneously reduces channel diameter and internal volume. Consequently, the ethylene selectivity is enhanced and the formation of coke precursors is restricted, resulting in improved stability.

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1. Introduction

As an important building block in the chemical industry, ethylene is principally produced by steaming cracking and fluid catalytic cracking of naphtha or gas oil [1]. However, with rising demand for ethylene, the capacity of such petrochemical cracking processes fails to meet the needs of manufacture of basic and intermediate chemical materials such as polymer and ethylene oxide [2,3]. Furthermore, owing to relatively high feedstock cost and low selectivity to ethylene, the naphtha-based process seems less competitive than that based on ethane, in which the conversion of hydrocarbon reaches 70% with yield up to 50% [2,4]. Discovery of a large reserve of shale gas has reignited wide interest in thermal cracking using natural-gas-derived ethane as feedstock. However, those pyrolysis processes suffer from high operating temperature and high equipment demand. Catalytic dehydrogenation of light alkanes that proceeds under milder conditions is a promising alternative to alleviate the issue of high energy consumption.

State-of-the-art routes developed for catalytic dehydrogenation of light alkanes include direct dehydrogenation to olefins and dehydroaromatization to aromatics [4–10]. As to direct dehydrogenation of ethane to ethylene, current research mainly involves Pt-based catalysts. Despite efforts to modify the electronic and geometric structure of Pt-based catalysts with promoters such as Sn, Ga, In, and Ir, the stability is still limited, primarily due to coke deposition [11–17]. Furthermore, the high temperature required for reaction and catalyst regeneration also provokes aggregation of Pt particles, leading to reduced activity [1,18]. A novel preparation protocol such as the atomic layer deposition method (ALD) has been proposed to annihilate active sites for hydrogenolysis or coking and sterically isolate and stabilize desired active sites, which could be beneficial in suppressing coking and sintering to prolong the catalyst life [19,20]. The formidable issue associated with the nonoxidative catalytic conversion of ethane to ethylene lies in its limited equilibrium conversion, which makes it less economically attractive [2,4,19,20].

In comparison with direct dehydrogenation to olefins, dehydroaromatization exhibits a higher equilibrium conversion in the same temperature range [5]. The exemplary Cyclar process developed by BP-UOP is based on bifunctional catalysts, where an initial dehydrogenation product, such as ethylene, is produced on dehydrogenation sites and subsequent oligomerization and aromatization takes place on Brønsted acid sites [9,21]. However, the

paradox occurs that the higher acid density and strength indispensable for facilitating the conversion of ethane to aromatics also contribute to cracking and hydride transfer, leading to easier formation of methane and coke [7,9]. The reduction of acid density and strength would enhance the ethylene selectivity but lower the ethane conversion [5,9]. In all, obtaining a high ethylene yield via catalytic dehydrogenation of ethane on zeolite-based catalysts is highly challenging.

Mo/ZSM5 has been proven an effective catalyst for dehydroaromatization of methane [22–26]. Molybdenum species have been verified to exist in an isolated state after calcination in air; these are efficient in selective activation of C—H bonds but not stable and apt to agglomerate with time on stream [25,27]. Recently, it was shown that activity loss due to coke and aggregation of molybdenum species can be restored by air calcination [25,28]. However, Kosinov et al. pointed out that the dealumination due to interaction of Mo and framework aluminum under oxidative conditions at high temperature led to irreversible deactivation [29]. To date, there are few reports on conversion of ethane to ethylene or BTX (benzene, toluene, and xylene) catalyzed by Mo/ZSM5 and even fewer on the catalyst stability [8]. Here, we carried out a systematic study of Mo/ZSM5 for ethane dehydrogenation. High ethylene yield and catalyst stability with low carbon loss due to coke and methane formation were obtained on phosphorus-modified Mo/ZSM5. Particular attention was paid to understanding the influence of phosphorus on the catalyst structure and its correlation with the catalytic performance.

2. Experimental

2.1. Catalyst preparation

Mo/ZSM5 was prepared via a wet impregnation method adapted from our previous work [26]. Briefly, an aqueous solution of $(NH_4)_6Mo_7O_{24}$ was added to ZSM5 (purchased from Nankai University, $SiO_2/Al_2O_3 = 50$) with a nominal loading of 4.7 wt.% Mo. Then it was left at room temperature for 12 h and further dried at 110 °C for 12 h. Finally, the catalyst was calcined at 500 °C for 6 h. The obtained catalyst was denoted as Mo/ZSM5. Phosphorus was introduced by impregnating $NH_4H_2PO_4$ onto Mo/ZSM5 following the same procedure as for Mo/ZSM5 except for calcining at 600 °C for 3 h. Two different P loadings were prepared, namely 1 wt.% (denoted as 1P-Mo/ZSM5) and 2.5 wt.% (2.5P-Mo/ZSM5).

Silylation was carried out as described in a previous report [30]. Mo/ZSM5 or P-Mo/ZSM5 was added to 50 ml ethanol containing a desired volume of tetraethoxysilane (TEOS). After evaporation of ethanol at 60 °C, the sample was calcined at 550 °C for 4 h. The product was denoted as xSi Mo/ZSM5, with x representing the loading of SiO_2.

2.2. Catalyst characterization

NH_3 TPD was performed on an Auto Chem 2910 with a TCD detector. The temperature was raised to 800 °C at 10 °C/min. IR was carried out on a BRUKER TENSOR27 with pyridine as a probe molecule. The self-supported sample wafer was kept at 200 °C under vacuum for 1 h before absorption of pyridine at room temperature. The signal was collected at room temperature after the sample was evacuated at 150 °C for 30 min and then cooled down under vacuum. The ratio of Brønsted and Lewis acidity sites was determined using previously reported molar extinction coefficients [31]. The UV–visible diffuse reflectance spectra (UV–vis DRS) were recorded on a JASCO V-550 spectrophotometer in the range 190–900 nm. A Bruker Avance III 600 MHz spectrometer with a Bruker 4 mm HXY MAS NMR probe operating at 600.13 MHz for ^1H, 156.4

MHz for ^{27}Al, and 242.9 MHz for ^{31}P was used for magic angle spinning (MAS) NMR spectra with the MAS rate at 12 kHz. Tetramethylsilane (TMS) (0 ppm), 1 M $Al(NO_3)_3$ (0 ppm), and $NH_4H_2(PO_4)_3$ (0.9 ppm) were used as external chemical shift standards for ^1H, ^{27}Al, and ^{31}P, respectively. The ^{27}Al 3Q MAS experiments were performed using a three-pulse sequence incorporating a z-filter at a MAS speed of 13 kHz. ^{129}Xe NMR was carried out at a Larmor frequency of 110.6 MHz on a Bruker Avance-400 spectrometer. XPS was performed on a Thermo ESCALAB 250Xi. Nitrogen physisorption was performed with a Quantachrome Autosorb-iQ2 gas adsorption analyzer. The specific surface area was calculated with the Brunauer–Emmett–Teller (BET) equation using the adsorption data ($p/p_0 = 0.05$–0.25). The volume and size of micropores were determined by the Saito-Foley (SF) method [32].

2.3. Catalytic reaction

The reaction was carried out at atmospheric pressure in a quartz microreactor with an inner diameter of 10 mm. A sample of 500 mg catalyst was loaded and heated up to 600 °C under Ar (30 ml/min) within 1 h. The feed gas contained 10% ethane, 10% N_2, and 80% He, with N_2 as the internal standard. The total gas space velocity was 5000 ml/g_{cat}/h. The product was analyzed with an online gas chromatograph (GC) (Agilent 7890A) equipped with an FID detector with an HP-1 capillary column and a TCD detector with a Hayesep D packed column. In addition to ethylene and BTX, minor products such as C_3 and naphthalene were also detected. The conversion of ethane and each product selectivity were calculated with N_2 as internal standard following the equations

$$\text{Conv.} = \frac{F^{\text{inlet}} \times X_{\text{ethane}}^{\text{inlet}} - F^{\text{outlet}} \times X_{\text{ethane}}^{\text{outlet}}}{F^{\text{inlet}} \times X_{\text{ethane}}^{\text{inlet}}}, \tag{1}$$

$$S(i) = \frac{N_i^{\text{carbon}} \times F^{\text{outlet}} \times X_i^{\text{outlet}}}{2 \times \left(F^{\text{inlet}} \times X_{\text{ethane}}^{\text{inlet}} - F^{\text{outlet}} \times X_{\text{ethane}}^{\text{outlet}} \right)}, \tag{2}$$

where F with superscripts "inlet" and "outlet" represents the total gas flow rate at the inlet and outlet of the reactor, respectively, X is the mole fraction of each component, and N_i represents the carbon number of the corresponding product i. Then the selectivity of coke was calculated on a carbon basis:

$$S(\text{coke}) = 1 - \sum_i S(i). \tag{3}$$

3. Results and discussion

3.1. Catalytic performance of P-Mo/ZSM5

Fig. 1 shows that modification with P had an obvious effect on the catalytic performance. Compared with Mo/ZSM-5, the initial ethane conversion over 1P-Mo/ZSM-5 increased significantly from 24.0% to 44.1%. However, it still dropped drastically from 44.1% to 12.5% within 260 min (Fig. 1a). In contrast, 2.5P-Mo/ZSM5 exhibited totally different behavior, as its activity rose quickly from 4.4% to 19.5% within 35 min. Then it almost leveled off within 200 min and subsequently slowly decreased from 19.5% to 16.4%. An induction period has been reported previously to be present in dehydroaromatization of methane due to the gradual reduction of Mo and formation of active centers [33,34]. In the case of 2.5P-Mo/ZSM5, a palpable induction period was also observed. Yet in contrast with Mo/ZSM5 in the dehydroaromatization of methane, 2.5P-Mo/ZSM5 was much more stable. This indicated a significant role of P in improving the catalyst stability.