Enhanced performance of boron nitride catalysts with induction period for the oxidative dehydrogenation of ethane to ethylene

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A B S T R A C T

Hexagonal boron nitride (h-BN) has recently aroused continuous interest in the oxidative dehydrogenation (ODH) of light alkanes. Here we found that commercial h-BN exhibits an induction period during the ODH of ethane to ethylene. It can achieve better performance only on activated BN after the first cycle run of ODH or treatment of reactants together. The conversion of ethane was 36% at a selectivity of 79% on the activated BN at 570 °C, which nearly tripled that on the fresh BN (12% conversion with 84% selectivity). An excellent productivity of 110 μmol g_{cat}^{-1} s^{-1} was obtained, which was one order of magnitude higher than that on most previous catalysts. Various methods of characterization such as infrared spectroscopy, O_2 adsorption microcalorimetry, and transient analysis of products by mass spectroscopy indicated the formation of B–OH species on BN after the induction period. There was a linear relationship between the reaction rate of ethane and the quantity of OH species. It is suggested that B–OH species can facilitate the adsorption of O_2 and then be transformed to B–O species, which would react with ethane to produce ethylene with the assistance of O_2, thus resulting in a higher reaction rate and a lower activation energy.

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1. Introduction

Ethylene (C_2H_4) is one of the fundamental building blocks in the chemical industry for the synthesis of polymers, plastics, fiber, vinyl chloride monomers, ethylene oxide, functionalized hydrocarbons, and other chemical products [1]. In 2016, the total demand for C_2H_4 reached 153 million tons all over the world and the net added demand was expected about 5.2 million tons every year [2]. Nowadays, the steam cracking of naphtha and ethane is still the primary process for the industrial manufacture of C_2H_4 despite the rapid development of methanol-to-olefins (MTO) technology [3,4]. Particularly, the discovery of huge volumes of natural gas and shale gas can provide abundant ethane [5]. Nevertheless, the shortcomings of steam cracking are obvious, including thermodynamic constraints, high operating temperatures (usually >800 °C), and large energy demand [6]. In recent years, attention has been paid to finding other economic and environmentally friendly routes, in which the oxidative dehydrogenation (ODH) of ethane ($C_2H_6 + 0.5O_2 \rightarrow C_2H_4 + H_2O$, $\Delta H = -104.9$ kJ mol^{-1}) is one of the most promising routes. This process is highly desirable due to its exothermic properties with low energy consumption, as well as the absence of thermodynamic limitations and coke formation [7].

However, ethylene tends to be more active than ethane, as the electron-rich ethylene more easily bonds with the catalytic surface directly, whereas ethane interacts almost exclusively through dispersion forces [8]. Therefore, the scientific challenge for the ODH reaction is the prevention of ethylene overoxidation to thermally stable CO_2 and H_2O. Up to now, various formulations of catalysts have been explored. According to the type of active species, they can be classified as supported metal catalysts, complex oxides, metal chlorides, and nonoxides. The Pt-based catalysts such as Pt and Pt–Sn exhibit higher conversion and selectivity after the addition of H_2 during the ODH of ethane at much shorter contact times than steam cracking [9–13]. The oxide catalysts, especially MoVTeNbO [14–17] and NiMO catalysts [18–22] (M is a doped metal with higher valence than Ni), show excellent performance at temperatures below 450 °C. However, the formation of O_2^- or O^- can lead to easy overoxidation [8]. In contrast, the oxides with chloride modification such as Li-K-Cl/MgO + Dy_2O_3 or the recently reported EuOCl can maintain 90% selectivity to ethylene at high ethane conversion (>80%) [23,24]. It was found that the Cl ion played an important role in the activation of O_2, while deactivation occurred with increasing temperature due to the loss of Cl [25]. On the other hand, nonoxides such as carbon nanotubes have been also studied in the ODH of butane and ethylbenzene [26]. However, they work only at low temperature (400 °C) and exhibit low activity (<3%)

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in the ODH of ethane due to the combustion of carbon material at higher temperatures [27].

Boron nitride, a structural analogue of graphene, has attracted increasing attention in the past five years [28]. This material exhibits superior thermal and chemical stability, high oxidation resistance, and high thermal conductivity. In the study of catalysis, it usually is a support for highly dispersed metal species such as Au, Ni, and Pt [29–31]. Bulk BN usually exhibits much inferior performance due to the lack of unsaturated coordinative sites [32,33]. Very recently, Grant et al. first reported the application of h-BN and BN nanotubes in the ODH of propane to propene, which showed better selectivity at higher conversion than state-of-the-art catalysts [34]. Thereafter, BN hydroxylated by Na-assisted high-temperature steam activation or high-surface-area BN with the specific morphology of nanosheets or carbon-doped BN nanosheets was explored as a means to improve the selectivity of alkane to olefin [35–37]. In contrast to the complicated preparation and control of special morphology, there was still room to improve the conversion and selectivity for the ODH of ethane over ordinary BN from commercial sources. Moreover, the structure–activity relationship during the ODH reaction also needed further description. In this work, it was found that commercial h-BN exhibits an obvious induction period during the ODH of ethane. Only the catalyst that was activated by the reactants together can achieve better activity, selectivity, and stability. Various characterizations were then employed to illustrate the factors in the high performance of this activated BN catalyst.

2. Experimental

2.1. Materials and treatments

Commercial hexagonal boron nitride (h-BN) was purchased from Alfa Aesar China Co. The BN sample without any chemical or thermal treatment was named fresh BN. The BN sample that was pretreated at 600 °C for 2 h in feed gases (10 vol% C_2H_6 and 5 vol% O_2 diluted in He) was denoted as activated BN. For comparison, the BN sample was also treated under various oxidative or reductive atmospheres at 600 °C for 2 h, such as 10 vol% H_2, 10 vol% O_2, 10 vol% H_2O, and 10 vol% C_2H_6 (He as the balance gas), which were named H_2-treated BN, O_2-treated BN, H_2O-treated BN, and C_2H_6-treated BN, respectively.

2.2. Catalytic performance test

The catalytic performance was evaluated in a fixed-bed reactor (i.d. 8 mm) at atmospheric pressure in the temperature range 530–600 °C. A quantity of 0.1 g of catalyst diluted with 0.5 g of SiO_2 was introduced into the reactor with quartz wool as support. The feed gases consisted of 10 vol% C_2H_6, 5 vol% O_2, and 2 vol% N_2 (used as an internal standard) and were balanced with He under a total flow rate of 30 mL min^{-1}. The reactants and products were analyzed by an online gas chromatograph equipped with a TCD and two columns: a Pora PLOT Q column for analyzing CH_4, CO_2, ethane, and ethylene and a molecular sieve 5A column for analyzing H_2, O_2, N_2, and CO. The conversion of ethane and the selectivity to ethylene were calculated on a carbon basis with the carbon mass balance above 95% in all cases. A blank experiment on 0.5 g SiO_2 was carried out under the same conditions.

2.3. Catalyst characterization

X-ray diffraction (XRD) measurements were recorded on a PW3040/60 X'Pert PRO (PANalytical) diffractometer using a CuKα radiation source (λ = 0.15432 nm, 40 kV, 40 mA). A step-scan mode was used to collect data in the 2θ range from 10° to 80° at a scanning speed of 5° min^{-1}.

N_2 adsorption/desorption isotherms were collected on an ASAP 2460 Quantachrome instrument. The samples were degassed under vacuum for 4 h at 300 °C before measurement. The surface areas of the samples were calculated by the BET (Brunauer–Emmett–Teller) equation.

Thermogravimetric analysis (TGA) was performed on SDT Q600 in air with a constant flow rate of 100 mL min^{-1}. The measured temperature ranged from 50 to 800 °C with a ramp rate of 10 °C min^{-1}.

The morphology of the catalyst was detected on a JSM-7800F scanning electron microscope (SEM). High-resolution transmission electron microscope (HRTEM) images were obtained on a JEOL 2100FS STEM/TEM instrument.

The Fourier transform infrared (FTIR) spectra of the fresh and activated BN catalysts were obtained in the transmission mode on a Bruker Equinox-55 infrared spectrometer at a resolution of 4 cm^{-1}. The fresh BN catalysts were pretreated withy feed gases at 575 °C for 1, 1.5, 2, 3, and 4 h. After that, these catalysts were removed from the reactor and diluted with KBr (mass ratio KBr:BN = 30:1) at room temperature and atmospheric pressure. In another experiment, the fresh BN and the ones that were activated by feed gases at different temperatures (550, 570, 580, and 600 °C) for 2 h were also measured under the same conditions.

O_2 adsorption microcalorimetry was performed on a BT 2.15 heat-flux calorimeter (Seteram, France). The calorimeter was connected to a gas handling and volumetric system using MKS 698A Baratron capacitance manometers for precision pressure measurement. Prior to the adsorption, the fresh BN was treated with He at 600 °C for 1 h and vacuumed in a special treatment cell. The activated BN was obtained by treatment in feed gases at 600 °C for 2 h and in He for 1 h, followed by evacuation for 30 min. The adsorption experiment was conducted at 40 °C and the detailed procedures for microcalorimetric adsorption have been reported previously [38].

In situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) was performed on the activated BN under different atmospheres with a constant flow (30 mL min^{-1}). In detail, the activated BN after purging with He at 550 °C for 1 h was cooled down to room temperature and recorded as background. Then it was treated with 1 vol% O_2 at 550 °C for 1 h and cooled to room temperature under He. Afterward, it was treated stepwise with 2 vol% C_2H_6, 1 vol% O_2, and finally 2 vol% C_2H_6 + 1 vol% O_2. All the spectra were measured under He in the steady state.

Transient analysis of surface reactions was performed in a fixed-bed reactor by detecting the outlet gases with an online mass spectroscope (MS). The gate time for MS analysis was 0.1 s for each component (C_2H_6, C_2H_4, O_2, H_2O). Typically, 0.1 g of the activated BN was placed in the reactor and purged with He for 1 h at 550 °C. The dynamic evolution of effluent gas was investigated by switching gas from He to 1 vol% O_2, 2 vol% C_2H_6, 1 vol% O_2, and finally 2 vol% C_2H_6 + 1 vol% O_2. These experiments were performed sequentially; the time schematic is described in detail in Fig. S1 in the Supporting Information. The flow rate was maintained at 30 mL min^{-1}. The MS signals of C_2H_6, C_2H_4, O_2, and H_2O were obtained until the steady state was reached with the noise removed by the experiment in the blank reactor.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcat.2018.05.023.

3. Results

3.1. Catalytic performance

Fig. 1a displays the conversion of C_2H_6 over the fresh and activated BN as a function of reaction temperature. There is almost no