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Selective oxidative dehydrogenation of ethane to ethylene over a hydroxylated boron nitride catalyst

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ABSTRACT

Boron nitride containing hydroxyl groups efficiently catalysed oxidative dehydrogenation of ethane to ethylene, offering rather high selectivity (95%) but only small amount of CO₂ formation (0.4%) at a given ethane conversion of 11%. Even at high conversion level of 63%, the selectivity of ethylene retained at 80%, which is competitive with the energy-demanding industrialized steam cracking route. A long-term test for 200 h resulted in stable conversion and product selectivity, showing the excellent catalytic stability. Both experimental and computational studies have identified that the hydrogen abstraction of B-OH groups by molecular oxygen dynamically generated the active sites and triggered ethane dehydrogenation.

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1. Introduction

Ethylene is one of the most important building blocks in chemical industry, with a global production capacity of 120 million metric tons per year [1]. Currently, the industrialized process for ethylene production is steam cracking of petroleum- and/or natural-gas-derived hydrocarbons at high-temperatures (approximately 800 °C), inevitably involving tremendous energy consumption and significant emission of CO₂ (1–1.6 ton CO₂ per ton of ethylene) [2,3]. In addition, notable amount of carbon deposit formed under such harsh reaction conditions will cover the alloy tubes and halt the reaction, thus requiring frequent regeneration for cleaning the deposited coke [4].

Oxidative dehydrogenation (ODH) of ethane to ethylene represents a promising alternative to steam-cracking process,

because of the favorable thermodynamic and kinetic characters, for example, exothermic, lower reaction temperature, faster reaction rate, and almost no coking [5,6]. In the past decades, this reaction has widely developed using the metal-based catalysts [7–9]. To date, the catalytic systems that could offer good performance mainly include Pt/Sn, SrFeO_{3-δ}Cl_δ, Mg/Dy/Li/Cl/O, and MoVTenbO_x [2,4,10,11]. However, deep-oxidation over these metal-based catalysts caused significant decrease in the selectivity of ethylene [12]. Nanostructured carbon materials, representing one type of metal-free catalysts, have been shown as a competitive system in the ODH of hydrocarbons, but with very low conversion of ethane and propane at the temperature up to 500 °C [13,14]. It is most likely that in the case of ODH of ethane, typically operating at 500–700 °C, carbon materials are fatally oxidized to CO₂.

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Boron nitride, also a type of metal-free catalysts, is characterized by the excellent structural and thermal stability under oxidative atmospheres [15,16]; and it has been demonstrated, quite recently, to selectively and efficiently catalyze the ODH of propane to propylene in the temperature up to 500 °C [17]. Independently, our group demonstrated that hydroxylated boron nitride can selectively oxidize propane to propylene with long reaction stability and extremely low CO₂ formation [18]. As the ODH of ethane typically operates at higher temperatures than that of propane, catalysts with outstanding high-temperature oxidation resistance become the crucial issue. Herein, we report that hydroxylated boron nitride (BNOH) can efficiently catalyze the ODH of ethane to ethylene, offering rather high selectivity of ethylene (up to 95%) and excellent stability for 200-h test.

2. Experimental

2.1. Catalyst preparation

The boron nitride was hydroxylated by a sodium-assisted high-temperature steam activation process. Initially, sodium nitrite solution (200 µL, 1 mol L⁻¹) was incipient impregnated into boron nitride (1.0 g), followed by calcination in air at 560 °C for 1 h. The solid product was then treated at 530 °C with 5 vol% H₂O/N₂ for 3 h. Sodium ions were further leached out with a reflux in 3 mol L⁻¹ ammonia at 80 °C for 3 times, followed extensive washing with ultrapure water (40 times, 50 mL water each). The obtained powders were treated in air at 500 °C for 2 h. The obtained sample was named as BNOH.

2.2. Catalytic evaluation

Catalytic reactions were performed in a fixed-bed microreactor. The feed consists of C₂H₆/O₂/N₂ with a molar ratio of 1/1/4, and flow rate of reaction gas was fixed at 48 mL min⁻¹. The reaction temperature was varied in 550–610 °C. The reaction products were analyzed by online gas chromatograph equipped with a TCD. A GDX-102 and molecular sieve 5A column were used to analyze the O₂, N₂, C₂H₆, C₂H₄, CH₄, CO, and CO₂. In kinetic analysis, the dependence of ethane conversion on reaction temperature was evaluated to calculate the apparent activation energy. Effect of contact time on reaction rate and product distribution was measured by varying reactant flow rates. Reaction orders were obtained by evaluating the effect of reactant partial pressure on reaction rates.

Conversion was defined as the number of moles of carbon converted divided by the number of moles of carbon present in the feed. Selectivity was defined as the number of moles of carbon in the product divided by the number of moles of carbon reacted. The carbon balance was checked by comparing the number of moles of carbon in the outlet stream to the number of moles of carbon in the feed. Under our typical evaluating conditions, the carbon balance was within ±5%. In order to account for the volume expansion in the reaction, nitrogen was used as the internal standard.

2.3. Catalyst characterization

X-ray diffraction (XRD) were measured on a PANalytical Model X'Pert 3 Powder diffractometer using Cu K_α radiation (λ = 0.15406 nm). High-resolution transmission electron microscope (TEM) measurements were performed on an FEI F30 microscope. Solid-state ¹H nuclear magnetic resonance (NMR) spectra were recorded on an Agilent DD2-500 MHz spectrometer at 499.8 MHz using a 4-mm MAS NMR probe with a spinning rate of 10 kHz. The chemical shifts were referenced to tetramethylsilane (TMS). Prior to testing, the sample was dehydrated at 400 °C for 1 h at 10⁻⁴ Pa. X-ray photoelectron spectroscopy (XPS) analysis was carried out on Thermo VGE SCALAB250 analyzer. Monochromatic Al K X-ray source (1486.6 eV, anode operating at 15 kV and 150 W) was used as incident radiation. The binding energy of the element was calibrated using an C 1s photoelectron peak at 284.5 eV. Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet 6700 FT-IR spectrometer equipped with a quartz transmission cell. The gas composition at the reactor outlet during FT-IR experiments was controlled by online mass spectrometry (Pfeiffer, OminStar™). Isotope-labelling experiments were carried out in a fixed bed microreactor. Initially, BNOH was treated at 590 °C in He (40 mL min⁻¹) for 1 h, and then a 12-h H/D exchange was performed in a 3.5 vol% D₂O/He stream. The BNOH after exchange was further purged using the dry He for 3 h. Subsequently, C₂H₆, O₂ or a mixture of the two (800 µL each time) was pulsed into the deuterated BNOH with He as the carrier gas. The chemical and isotopic compositions of the reactor effluent were measured by online mass spectrometry.

2.4. Computational details

All stationary points were fully optimized using the B3LYP hybrid exchange-correlation functional as implemented in Gaussian 09 program with all atoms described by a double ξ quality basis set, 6-31G(d, p), followed by vibrational frequency analysis to identify the nature of the stationary points, either as minima or transition states. Intrinsic reaction coordinate (IRC) calculations were carried out to confirm that each transition state connects the two minima along the reaction pathway.

3. Results and discussion

ODH of ethane was performed in a packed-bed quartz microreactor under atmospheric pressure using a feed gas containing ethane, oxygen and nitrogen (1:1:4). The BNOH catalyst afforded surprisingly high selectivity and yield toward ethylene. For example, the selectivity to ethylene was as high as 95% at 11% ethane conversion, the byproduct consisted of CO (4.7%) and CO₂ (0.4%) (Fig. 1(a)). As the conversion of ethane was increased to ~40%, the selectivity of ethylene still was kept at 90%, which was superior to that over most of metal and metal oxide catalysts [7]. As further increasing the conversion of ethane to 63% by raising the reaction temperature, the selectivity of ethylene only slightly lowered to 80%, correspond-

Fig. 1. ODH of ethane over the BNOH catalyst. (a) Dependence of ethane conversion, ethylene selectivity and yield on the reaction temperature; (b) Effect of space velocity and reaction temperature on the productivity of ethylene; (c) Long-term stability test at 590 °C. Reaction conditions: catalyst, 100 mg; gas feed, 16.7 vol% C₂H₆, 16.7 vol% O₂, and N₂ balance; 570–610 °C; space velocity 6.4–32.0 g_{C₂H₆} g_{cat}⁻¹ h⁻¹.

ing to an ethylene yield of ~50%. This outstanding performance renders BNOH a comparable system with well-developed ethane steam cracking process in view of the ~85% selectivity to ethylene at ~60% conversion of ethane, but much superior considering the much lower reaction temperature and CO₂ emission [2].

Notably, only negligible amount of CO₂, as the over-oxidation product, was formed over the BNOH catalyst even when ethane conversion reached 63% (Fig. 1(a)), clearly showing the excellent performance of the current BNOH catalyst in selective activation of the C–H bond in ethane. The effect of contact time on product distribution in ethane ODH further revealed that ethylene was the only primary product at the near-zero contact time, while selectivity to the byproduct CO approached to zero, evidencing that the BNOH catalyst intrinsically avoids the cleavage of C–C in ethane under the ODH conditions.

The BNOH catalyst also can afford high ethylene productivity, (i.e., grams of C₂H₄ formed per gram of catalyst per hour). As shown in Fig. 1(b), an unprecedented ethylene productivity (9.1 g_{C₂H₄} g_{cat}⁻¹ h⁻¹) with >90% selectivity was achieved over the BNOH catalyst by mediating the reaction conditions. Such productivity far exceeds the critical value, 1 g_{C₂H₄} g_{cat}⁻¹ h⁻¹, which would be commercially attractive [7]. The remarkable stability of the BNOH catalyst in the ODH of ethane was evidenced by the operation for 200 h at 590 °C, during which no obvious variations in the conversion and product selectivity was detected (Fig. 1(c)), demonstrating its potential for industrial application.

Structure evolution of the BNOH catalysts before and after ODH of ethane was characterized. XRD pattern (Fig. 2(a))

showed that the BNOH catalyst still retained the typical hexagonal layered structure after a 200-h reaction. As observed by TEM, the morphology and lattice fringe of the spent BNOH catalyst kept similar as the original ones (Fig. 2(b)). XPS analysis revealed that 8.3 atom% surface oxygen present in the spent BNOH catalyst, slightly higher than that (6.9 atom%) of the fresh one (Fig. 2(d)). Solid-state ¹H NMR spectra further revealed that the amount of B–OH groups in the BNOH catalyst remained unchanged even after a 200-h reaction test (Fig. 2(c)). These results further confirm that the BNOH catalyst is stable under the ethane ODH reaction conditions.

Furthermore, we tracked the dynamic evolution of B–OH groups under the ethane ODH reaction conditions using the FT-IR spectroscopy. As seen in Fig. 3(a), the characteristic band of hydroxyl stretching vibration was clearly observed at ~3400 cm⁻¹ [17–20]. Upon exposure to C₂H₆ atmosphere at 590 °C, the band position of the hydroxyl stretches remained unchanged (Fig. 3(a)), and no ethane conversion was detected. With the addition of molecular oxygen (O₂/C₂H₆/N₂), however, the absorption of hydroxyl vibrational stretches gradually weakened (Fig. 3(a)), accompanied with the formation of ethylene, indicating that the OH groups interacted with molecular oxygen and incorporated into the reaction system. The intensities of hydroxyl vibrational stretches were recovered upon steam activation (Fig. 3(a)), suggesting that the OH groups could be readily regenerated.

Isotope-labelling experiments further confirmed the catalytic role of the B–OH groups in ethane ODH reaction. When only O₂ was pulsed into the deuterated BNOH(D) catalyst at 590 °C, no species containing H or D atom were detected, suggesting that no activation of molecular oxygen occurred on the

Fig. 2. XRD patterns (a), high-resolution TEM images (b), ^1H NMR spectra (c), and B 1s, N 1s, and O 1s XPS spectra (d) of the fresh and spent BNOH catalyst after a 200-h test.

Fig. 3. (a) FT-IR spectra of B-OH vibration over the BNOH catalyst under C_2H_6 , $\text{C}_2\text{H}_6/\text{O}_2/\text{N}_2$ and $\text{H}_2\text{O}/\text{N}_2$ atmospheres at 590 °C. Mass spectra of C_2H_4 , H_2O , HD O and D_2O species upon pulsing C_2H_6 (b) or a mixture of C_2H_6 and O_2 (c) onto the deuterated BNOH(D) catalyst at 590 °C.

surface B-OH(D) group. Similarly, no product appeared as well when only pulsing C_2H_6 into the deuterated BNOH(D) catalyst (Fig. 3(b)), indicating no chemical interaction between C_2H_6

and surface B-OH(D) groups, and revealing the bridging oxygen bonded at the BNOH edge being unreactive for the ethane C-H activation. In contrast, when a mixture of C_2H_6 and

Fig. 4. Effect of partial pressures of oxygen and ethane on the converting rate of ethane (a,b), and the selectivity to ethylene (c,d) in ODH of ethane over the BNOH catalyst. Reaction conditions: catalyst 100 mg; gas feed 0–25.2 vol% C_2H_6 , 0–25.2 vol% O_2 , and N_2 balance; 590 °C; space velocity 12.8 $\text{g}_{\text{C}_2\text{H}_6} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$; 0.1 MPa.

O_2 was pulsed into the reaction chamber, besides the formation of ethylene and H_2O , both HDO and D_2O were also generated immediately (Fig. 3(c)), clearly indicating that the H/D atoms in the BNOH(D) catalyst were abstracted during the ODH reaction process. In subsequent pulses, the intensities of HDO and D_2O gradually decreased whilst the intensity of H_2O increased (Fig. 3(c)). This experiment verified the dynamic exchange between the H atoms in ethane and the edge of BNOH catalyst and the B–OH groups as the active sites.

In line with this, kinetic experiments were performed to obtain deep insights on the reaction pathway of ethane ODH over the BNOH catalyst. Fig. 4 shows the effect of reactant concentrations on the converting rate of ethane. Langmuir-type (L-type) dependence on oxygen concentration corresponds with a reaction mechanism controlled by O_2 activation on the catalyst surface (Fig. 4(a)), which is consistent with the observations by FT-IR and isotope-labelling experiments. The second-order dependence on ethane concentration suggested that gaseous ethane might react directly with the activated oxygen species on the catalyst surface (Fig. 4(b)). The increase in selectivity as increasing oxygen concentration (Fig. 4(c) and (d)) reveals that molecular oxygen favors the formation of ethylene. The apparent activation energy of ethane was estimated to be 241.7 kJ mol^{-1} . These kinetic behaviors are intrinsically different from traditional metal oxide catalysts which typically follow the Mars-Van Krevelen mechanism [21,22].

Based on catalytic, spectroscopic and kinetic data, density functional theory (DFT) calculations were further performed to understand the underlying possible reaction pathway. All

computational details and results were presented in Fig. 5. Based on the experimental studies, the hydroxylated boron nitride was considered as the resting state of the catalyst. In the presence of O_2 at high temperature, the edge B–OH groups may be dehydrogenated by O_2 , leading to the generation of two radical species, $\text{BNO}^\bullet$ and $\text{HO}_2^\bullet$ radicals with a free energy barrier of 2.06 eV and endothermicity of 1.80 eV. The $\text{BNO}^\bullet$ radical displays reactivity towards the hydrogen abstraction of ethane to produce $\text{C}_2\text{H}_5^\bullet$ radical. The free energy barrier was calculated to be 0.10 eV and the reaction is exothermic by 0.54 eV. The subsequent dehydrogenation of $\text{C}_2\text{H}_5^\bullet$ radical, either by O_2 or H_2O_2 , offers the primary product, C_2H_4 . Along this pathway, the

Fig. 5. Free energy profile of ODH of ethane catalyzed by BNOH from DFT calculations (IS: initial state; TS: transition state; FS: final state). Green represented boron, pink for nitrogen, red for oxygen, dark grey for carbon and light grey for hydrogen.

Graphical Abstract

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Selective oxidative dehydrogenation of ethane to ethylene over a hydroxylated boron nitride catalyst

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Hydroxylated boron nitride, a metal free catalyst, shows superior selectivity and excellent stability for the oxidative dehydrogenation of ethane to ethylene with only negligible CO₂ emission.

dehydrogenation of the B–OH sites appears as the rate-determining step. The HO₂[•] radical, either formed by the oxidation of BNOH or C₂H₅[•], may also be involved in the dehydrogenation of ethane via a free energy barrier of 0.93 eV. Accordingly, molecular oxygen plays crucial role in the ODH of ethane. It first abstracts one H atom from the BNOH to generate the BNO[•] active species and triggers the ODH of ethane, and it may also react with C₂H₅[•] to assist the formation of ethylene. This explains the L-type O₂-dependence observed in kinetic experiments (Fig. 4(a)). As seen in Fig. 4(a), (c), (d), increasing the partial pressure of O₂ favours the conversion of ethane and the selectivity to ethylene, suggesting the participation of O₂ in the consumption of the C₂H₅[•] intermediate to produce ethylene when sufficient amount of O₂ is present in the reaction chamber. Moreover, the activation pathway of ethane with edge BNO[•] and surface HO₂[•] species nicely support the second-order rate dependence with respect to ethane concentrations in the ODH reaction over the BNOH catalyst (Fig. 4(b)).

4. Conclusions

We demonstrate that boron nitride upon hydroxylation exhibits a superior selectivity to ethylene but only small amount of CO₂ formation in oxidative dehydrogenation of ethane. Based on experimental and computational studies, a possible reaction pathway was proposed that the hydrogen abstraction of B–OH groups by molecular oxygen dynamically generated the active sites, and triggered ethane dehydrogenation. This novel met-

al-free catalyst system enriches our knowledge on catalytic activation of alkanes and serves as a promising catalyst for the industrial ODH process.

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羟基化氮化硼催化乙烷氧化脱氢制乙烯

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摘要: 乙烯是最为重要的化工原料之一, 目前其工业来源主要来自于烃类的水蒸汽裂解过程. 该过程本质上是一个高温均相裂解过程, 温度(> 800 °C)高, 能耗大, 碳排放严重. 乙烷氧化脱氢制乙烯属于放热反应, 反应温度低, 速率快, 无积碳等限制, 是一条更富有竞争力的工艺路线. 然而, 常用的金属或金属氧化物催化剂容易导致乙烯深度氧化, 从而降低了乙烯选择性. 纳米碳材料在烃类氧化脱氢反应中展现出一定的催化活性, 但容易被氧化, 难以用于反应温度高的乙烷氧化脱氢反应.

本文报道了羟基化的氮化硼(BNOH)可高效催化乙烷氧化脱氢制乙烯. 氮化硼边沿羟基官能团脱氢生成了动态活性位, 从而引发了乙烷的脱氢反应. BNOH对乙烷氧化脱氢制乙烯显示出高选择性. 当乙烷转化率在11%, 乙烯选择性可高达95%; 当乙烷转化率增加到40%, 乙烯选择性保持在90%. 重要的是, 当乙烷转化率超过60%时, BNOH仍然可保持80%的乙烯选择性以及50%的乙烯收率. 这些性能指标与现有工业乙烷水蒸气裂解过程运行性能相当. 进一步优化反应条件, BNOH催化剂能够实现高达 $9.1 \text{ g}_{\text{C}_2\text{H}_4} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ 的时空收率. 经过200 h的氧化脱氢反应测试, BNOH催化剂活性和选择性基本恒定, 表明其具有非常好的稳定性. X射线粉末衍射结果显示, 反应前后BNOH催化剂的物相没有发生变化. 透射电子显微镜测试证实, 反应后BNOH催化剂的形貌和微观结构也没有明显改变. X射线光电子能谱结果显示, 反应200 h后BNOH催化剂表面的氧含量仅从反应前的6.9 atom%微增到8.3 atom%. ¹H固体核磁共振谱测试显示, 反应200 h后, BNOH催化剂上羟基含量无明显改变. 结合原位透射红外光谱和同位素示踪实验, 初步确定了BNOH催化剂上引发乙烷氧化脱氢反应的活性中心. 氮化硼边沿的氧官能团并不能引发乙烷的氧化脱氢反应, 而羟基官能团才是氧化脱氢反应发生的活性位. 在乙烷氧化脱氢条件下, 分子氧脱除羟基官能团上的氢原子动态生成BNO[•]和HO₂[•]活性位. 密度泛函理论计算表明, 乙烷首先在BNO[•]或HO₂[•]位活化生成乙基自由基, 这些中间物进一步与气相氧物种发生反应脱氢生成乙烯. 动力学测试结果也验证了上述实验和理论结果.

关键词: 氮化硼; 羟基化; 乙烷; 氧化脱氢; 乙烯

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