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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 CO_2 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 CO_2 (1–1.6 ton CO_2 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, $SrFeO_{3-\delta}Cl_\sigma$, 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 CO_2.

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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 hydroxlated boron nitride can selectively oxidize propane to propylene with long reaction stability ad extremely low CO_2 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% H_2O/N_2 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 $C_2H_6/O_2/N_2$ 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 O_2, N_2, C_2H_6, C_2H_4, CH_4, CO, and CO_2. 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 1*s* 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% D_2O/He stream. The BNOH after exchange was further purged using the dry He for 3 h. Subsequently, C_2H_6, O_2 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 CO_2 (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-

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