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Full Length Article

Thermal induced BCN nanosheets evolution and its usage as metal-free catalyst in ethylbenzene dehydrogenation

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ABSTRACT

Compared with mushroomed progress in metal-free C-rich BCN catalysts, little is known about the BN-rich BCN or even BN ones. Its related study has drawn great interest recently but still in its infancy stage. In this study, three kinds of BCN nanosheets (NSs) with tuned surface carbon contents (5.5–14.3%), specific surface area (SSA, 82–290 m^2/g) and morphologies (ultrathin nanosheets, triangular plates) were fabricated through a solid state reaction by simply adjusting the reaction temperature, and those effects on the ethylbenzene dehydrogenation performances were studied in CO_2 atmosphere. The morphology evolution of BCN NSs from ultrathin nanosheets to the triangular plates was observed and control experiments were carried out. The BCN nanosheets show relatively strong interaction with CO_2 and distinct CO_2 absorption properties. The CO_2 temperature programmed desorption also indicates that the desorption peaks of CO_2 are above 400 °C, enabling them potential CO_2 utilization catalysts. A weak association was found between the surface C contents and the catalytic performance as it normalized with SSA, and the B-O species could be taken as an active site in CO_2 atmosphere. Though much progress still needed, it is convincing that the BCN catalyst could be a promising metal-free catalyst in dehydrogenation beyond carbocatalyst.

1. Introduction

Being featured materials with high thermal stability, strong anti-oxidation properties and excellent thermal conductivity, *h*-BN has drawn special interest in heterogeneous catalysis in recent years [1–4]. It is an excellent catalytic material that can dissipates reaction heat in highly exothermic reactions, such as Fischer-Tropsch Synthesis, CH_4 combustion and deep oxidation of Volatile organic compounds (VOCs) [5–8]. The hydrophobic surface of BN can also drive off the condensed moisture in catalytic reactions, retarding the deactivation of catalyst, especially, no obvious deactivation was found for the Ba-Ru/BN catalyst even after 3500 h running for the ammonia synthesis [9]. Other than usage as support, heteroatom doping was supposed as an alternative route for high performance catalysts. Doping with other non-noble metal (Fe, Co) or even non-metal element (C, O, Si) were supposed another way to enhance their catalytic properties [10–12]. For example, the Be doped boron nitride meshes could play a determinant role in CO_2 conversion into hydrocarbon fuels [13].

As far as the C-doped BN nanosheets (BNNSs), so-called BCN nanosheets can form a layered hybrid structure because of their close lattice parameters. The C-doped BNNSs with a tuned medium band gap was therefore used as an excellent metal-free photoredox catalyst [4]. The BCN nanosheets with large specific surfaces area, rich of surface O-contains groups and featured defects (vacancies and edges) present outstanding durability and adsorption capacity and could be act as promising metal-free catalysts. The excellent carbon rich BCN nanosheets have been proved to be efficient metal-free oxygen reduction reaction (ORR) catalysts, even better than noble Pt/C catalyst [14]. The carbon rich BCN catalyst also showed excellent performances in dehydrogenation, and hydrochlorination of acetylene. The surface C=O related species was generally considered as an active sites.

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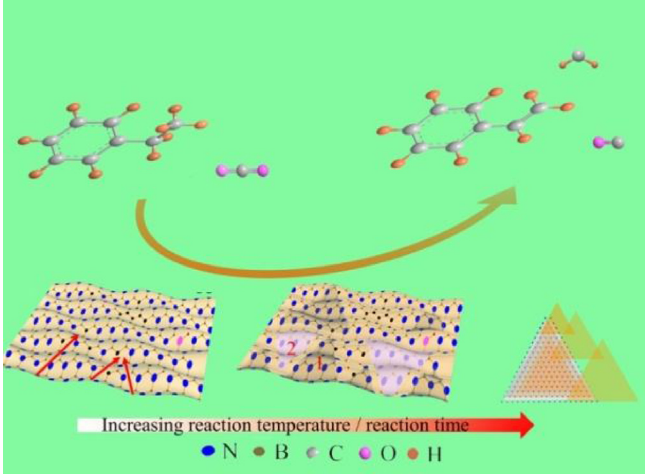

Scheme 1. BCN NSs as metal-free catalyst for the ethylbenzene dehydrogenation.

Compared with great progress in C-rich BCN catalyst, little is known about the BN-rich or even BN ones, yet. The theoretical study predicted the possibility of dehydrogenation by boron nitride catalyst over several years ago [15]. BNNSs show outstanding performances in hydrogenation of olefin [16]. Very recently, it reported that the BN and related catalyst act as an extraordinary metal-free dehydrogenation catalyst for the propylene and ethylbenzene (EB) above 400 °C in diluted O_2 [2,17,18]. Shi etc.al fabricates the OH terminated BN show an improved selectivity in propylene production [19], and the B-O and N—O was attributed to the active sites. However, its related study is still infancy. The usage of the molecular oxygen in those studies could leads to the deep oxidation and resulted in a reduced selectivity. The CO_2 was a soft oxidant, which was a promising alternative for stream used in industry, has drawn great research interest. Was the BCN catalyst active in the soft oxidant CO_2? Could the surface carbon plays as active site in the dehydrogenation as they do in both carbocatalysis and iron-based catalysis. Those questions need to be explored.

To study the catalytic ethylbenzene dehydrogenation performances of the BCN NSs in CO_2 and the effect of the surface C species, three kinds of BCN NSs with adjustable SSA, surface C contents and morphology were fabricated through a solid-state reaction in this study. The BCN NSs show a morphology evolution from ultrathin nanosheets to triangular nanoplates with the reaction temperature. The as-obtained BCN NSs show relatively strong interaction with CO_2, and their dehydrogenation performances in CO_2 atmosphere were studied (Scheme 1). Our study shows that the B—O species of the BCN NSs catalyst play dominant role compared with surface C species in CO_2 atmosphere.

2. Material and methods

2.1. Materials

All the reagents used in the experiments were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). NaN_3 was of CP grade; all the other reagents used were of AR grade.

2.2. Synthesis of BCN samples

Unless otherwise stated, the typical procedure was described as below. 30 mmol $NaBH_4$ were grounded with 40 mmol NaN_3 and placed into a stainless steel autoclave of 20 mL capacity. After 25 mmol alcohol was added, the autoclave was sealed and heated in an electric stove ramped at 10 °C/min to 400, 500 and 600 °C for 8 h, respectively. As it was cooled to room temperature naturally, the as-obtained powders were treated with alcohol and distilled water in sequence and finally 2 M HCl overnight. The samples were washed and dried at 60 °C. Then the samples were marked as BCN400, BCN500 and BCN600 based on their preparation temperature. As other reaction time and ethyl alcohol dosage was used, the alcohol dosage and reaction time was directly marked. For example, the sample BCN600–16 mmol indicated the dosage of ethyl alcohol was 16 mmol with other parameters unchanged in case of BCN600. The BCN600–1 h only indicates that the reaction time was 1 h with other parameters same.

2.3. Instrumental analysis

X-ray powder diffraction (XRD) measurements were conducted using a Bruker D8 advanced X-ray diffractometer (Cu Kα radiation, $\lambda = 1.5418$ Å). The morphology and structure of the products were investigated using transmission electron microscopy (TEM, Hitachi, H-7650) and high-resolution TEM (HRTEM, JEOL 2100). The Fourier transform infrared spectroscopy (FT-IR) was collected using a Nicolet IS50 spectrometer. Surface analysis of the samples was performed by an Axis Ultra DLD imaging photoelectron spectrometer (Kratos Analytical Ltd). The source of X-ray was Al Kα, 1486.6 eV with a quartz monochrometer. The specifc surface area was estimated using the Brunauer–Emmet–Teller (BET) equation based on the nitrogen adsorption isotherm (77 K) using a Tristar II (3020) instrument. The sample was degassed under vacuum at 180 °C for 6 h before measurement. The temperature Programmed Desorption was carried out under an Ar atmosphere at a heating rate of 10.0 °C/min^{-1} using a quadrupole mass spectrometer (OMNIstar GSD 301 O3; Pfeiffer Vacuum D-35614Asslar) as detector and was baseline corrected. Before the TPD analysis, the catalysts were degased at 300 °C over 2 h, then CO_2 steam was introduced at 104 °C over 1 h.

2.4. Catalytic testing

The dehydrogenation of ethylbenzene was carried out using a quartz tube reactor with an internal diameter of 8 mm and a height of 350 mm. Before the catalytic reaction, the catalyst was firstly pressed, ground and sieved to 40–80 mesh. The BCN NSs catalyst of 300 mg were diluted with 300 mg 40–80 mesh quartz sand, and then fixed by quartz sand. Before the catalytic reaction, the catalyst was treated with CO_2 for 120 min at 550 °C. Then, the dehydrogenation was performed at 550 °C under atmospheric pressure. The flow rate of ethylbenzene was fixed at 0.3 mL/min, and CO_2 of 19 mL/min. A wet gas flow meter was used to monitor the flow rate of tail gas. The products were condensed by a cold trap at 278 K and analyzed using flame ionization detector gas chromatograph (GC-950). The conversion of ethylbenzene (X_{EB}) and the selectivity to styrene (S_{ST}) as the criteria of catalytic performance were defined as the following equations.

$$X_{EB} = (1\text{-}EB_{out}/EB_{in}) \times 100 \tag{1}$$

$$S_{ST} = (\mathrm{productout}/(EB_{in} - EB_{out})) \times 100 \tag{2}$$

3. Results and discussion

3.1. Structural analysis

The structure of the as-prepared BCN NSs was firstly characterized by XRD, as shown in Fig. 1a. The diffraction peaks centred around 26.2° (3.38 Å) and 42.9° (2.12 Å) can be indexed as $(002)_h$ and $(100)_h$ plane based on the hexagonal phase (*h*BN or 2H graphite, JCPDS card no. 34-0421). The broad (002) peak of BCN400 and