Oxidative dehydrogenation of propane using layered borosilicate zeolite as the active and selective catalyst

Bin Qiu, Fan Jiang, Wen-Duo Lu, Bing Yan, Wen-Cui Li, Zhen-Chao Zhao, An-Hui Lu*

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, PR China

Abstract

Oxidative dehydrogenation (ODH) of propane to propylene offers a promising large-scale alternative to direct dehydrogenation. The reported metal oxides catalysts generally cause over-oxidation of propylene to COx, thus hindering the commercialization of ODH processes. In this study, a layered borosilicate zeolite was demonstrated as highly active and selective catalyst for the oxidative dehydrogenation of propane, showing a propylene selectivity of 83.6% and the total light olefins (propylene and ethylene) selectivity of 91.2% at a propane conversion of 3.9%. Further, at a propane conversion of 15.6%, the catalyst exhibited a propylene selectivity of 80.4% and the total light olefins selectivity of 91.6% at 530 °C. Structural characterization revealed that the abundance of defective trigonal boron species (B[3]a and B[3]b) was responsible for the activity of propane ODH.

1. Introduction

Oxidative dehydrogenation (ODH) of propane to propylene offers a promising large-scale alternative to direct dehydrogenation. The major advantages of ODH are the absence of equilibrium limitations on propane conversion and the suppression of catalyst coking [1–3]. Supported metal oxides [4–7], especially those based on VOx as the active sites, have been extensively studied as propane ODH catalysts in the past decades [8,9]. However, these catalysts generally cause over-oxidation of propylene to COx, thus hindering the commercialization of ODH processes.

Recently, several catalysts based on defective hexagonal boron nitride for the ODH of light alkanes have been reported. This new family of catalysts shows superior selectivity to olefins and low CO2 formation [10–12]. Our previous work revealed that oxygen-containing boron species at the surface of boron nitride are critical to their superior catalytic performance [13,19]. Hermans and co-workers proposed that amorphous oxidized boron layer were responsible for high activity in boron nitride [20] and the same conclusion was obtained in the supported B/SiO2 catalysts [21]. Inspired by the previous studies, besides boron nitride, thermally stable silicon boride has also been proved as the active catalyst for ODH [22]. Nevertheless, these catalysts are usually having low surface area. For heterogeneous catalysis, high surface area catalyst usually provides more active sites. Hence, the design of new catalysts with well dispersed boron using high surface area supports is desirable to further improve the catalytic performance.

Zeolites are one of the most common catalyst supports, and widely used in industry due to its large internal surface areas, micropores of molecular dimension, and high thermal stabilities [23,24]. In this study, we demonstrated that layered borosilicate zeolite (ERB-1, an MWW borosilicate zeolite) [25] was an active and selective catalyst for ODH of propane, showing a propylene selectivity of 80.4% at a propane conversion of 15.6%. Noticeably, the total selectivity to light olefins can reach 91.6% at 530 °C. The catalytic active sites were attributed to the abundant of defective trigonal boron structures.

2. Experimental methods

2.1. Catalyst preparation

The MWW borosilicate lamellar precursor was synthesized hydrothermally according to earlier report, with slight modifications [25]. First, 8.67 g hexamethyleneimine (HMI) was dissolved in 15.3 g deionized water with strong stirring at room temperature. Then, boric acid was added and the mixture was stirred for 1 h. Finally, silica sol (9.2 g) was added and then the mixture was stirred for another hour to obtain a gel with a molar composition of 1SiO2·xB2O3·1.4HMI·19H2O (x = 0.3, 0.5 and 1.0). The gel was sealed into a 50 mL Teflon-lined stainless steel autoclave and subjected to hydrothermal treatment at 175 °C under tumbling condition for 7 days. After cooling down to room temperature, the
product was filtered, washed, dried and finally calcined at 550 °C in air for 6 h to remove the templating agent. The materials are denoted BZE0-1, BZE0-2 and BZE0-3, accordingly with boron content 1.54 wt%, 2.48 wt% and 4.88 wt%. The used catalyst BZE0-2 (20 h-spent, 2.40 wt% B) was treated through washing and filtering with 600 mL deionized water, to obtain the sample denoted BZE0-2-W of which the boron content is determined as 0.85 wt%.

2.2. Catalyst characterization

The actual boron content of the zeolites before and after various treatments was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) on Optima2000DV. Before the measurements, the sample (10 mg) was dissolved by hydrochloric acid (3 ml) and hydrofluoric acid (3 ml) mixed solution in a teflon-lined autoclave at 150 °C for 1.5 h. After evaporating up the solution which contained hydrochloric acid and hydrofluoric acid, we repeatedly added deionized water into the teflon container and then collected the solution into a polypropylene volumetric flask, finally fixed the solution volume as 25 ml.

Powder X-ray diffraction (XRD) was recorded on PANalytical X'Pert3 Powder diffractometer using Cu Kα radiation (λ = 0.15406 nm). The zeolite powder was placed inside a quartz-glass sample holder for testing. The tube voltage was 40 kV, and the current was 40 mA.

N₂ adsorption-desorption isotherms were measured with an ASAP 2020 sorption analyzer (Micromeritics). Prior to the measurement, the sample was degassed by evacuation at 200 °C for 4 h. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area (S BET). Total pore volume (Vtotal) was calculated from the amount of gas adsorbed at a relative pressure P/P0 of 0.99. Micropore volume (Vmicro) was calculated using the t-plot method.

Transmission electron microscopy (TEM) images were recorded on a Hitachi HT7700, operating at an accelerating voltage of 120 kV. The scanning electron microscopy investigation were carried out with Hitachi FESEM SU8220 instrument.

IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer equipped with mercury cadmium telluride (MCT) detector. ¹¹B MAS NMR spectra were recorded on Agilent DD2-500 MHz spectrometer with an 11.7T magnet and Bruker AVANCE III 600 MHz spectrometer with a 14.1T magnet, using a 4-mm MAS NMR probe with a spinning rate of 10 kHz. Quantitative 1D MAS ¹¹B one pulse NMR spectra acquired at 14.1T were obtained with a small flip angle of π/12 at corresponding ¹¹B rf field of about 36 kHz with a recycle delay of 2 s [26]. Two-dimensional (2D) ¹¹B multiple-quantum (MQ) MAS NMR experiments were performed on Agilent DD2-500 MHz spectrometer using a three-pulse sequence incorporating a z-filter at a spinning speed of 10 kHz. The spectra were acquired with 1024 scans per increment, a recycle delay of 1 s. Chemical shifts were referenced to a 1 M H₃BO₃ aqueous solution at 19.6 ppm. The DMFIT program was used to deconvolute the spectra and fit the peaks [27]. The peak areas represented the amount of nuclear spins, i.e., the amount of corresponding B species; therefore, the relative amount of B species in each spectrum could be derived. We assumed that all B species were observed in the ¹¹B MAS NMR, and the amount of each species could be obtained for each sample with a given B content derived from ICP-OES. Considering the fact that under the ODH conditions, water molecules can be formed in situ, indicating that the environment of the catalysts located were not free of water. Therefore, when we measured the NMR spectra, we took our samples (that were stored after reactions under inert atmosphere) and packed them into NMR rotors, and then conducted the measurements at room temperature.

2.3. Catalytic tests of propane and ethane oxidative dehydrogenation

Selective oxidation of propane and ethane was studied in a fixed bed reactor (I. D. = 8 mm, length = 42 cm) packed with 200 mg catalyst (without diluent, 40–60 mesh) and heated to 500–590 °C under atmospheric pressure. Quartz wool was put in the middle of the reactor tube to support the catalysts. A thermocouple was inserted into the center of the catalyst bed to control the reaction temperature. The feed gas contains C₃H₈/O₂/N₂ with a volume ratio of 1:1.5:3.5 and C₂H₆/O₂/N₂ with a volume ratio of 1:1:4 at a fixed total flow rate of 48 ml/min. Reactants and products were analyzed using an online gas chromatograph (Techcomp, GC 7900) equipped with a GDX-102 and molecular sieve 5A column. A TCD was used to detect O₂, N₂, C₃H₈, C₂H₆, C₂H₄, CH₄, CO, and CO₂. 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. Under our typical evaluating conditions, the carbon balance was generally higher than 95%. The blank experiment was conducted using 200 mg quartz sand under the same reaction conditions.

3. Results and discussions

3.1. Structure and property of MWW borosilicate

Layered borosilicate zeolites were synthesized. Fig. 1a–c showed the SEM images of BZEO-1, BZEO-2 and BZEO-3 catalysts, and the BZEO zeolites were composed of intergrown, randomly-oriented, flaky crystals with particles of about 1–2 μm in length and around 100 nm in thickness. TEM image further revealed that the lamellar zeolite consisted of rectilinear sheets with a clear crystallized structure (Fig. 1d).

As seen in Fig. 2a, the X-ray diffraction (XRD) patterns showed four main diffraction peaks at 2θ = 7.21, 8.02, 10.10 and 26.33°, corresponding to the known (1 0 0), (1 0 1), (1 0 2) and (3 1 0) reflections of ERB-1, which confirmed the MWW structure [28]. The N₂ adsorption-desorption isotherms of different boron-containing MWW-type zeolites exhibited nearly type-I shape (Fig. 2b), featuring predominantly micropores with a small proportion of interstitial mesopores. Detailed information was listed in Table S1. The presence of boron in the framework was confirmed by the FT-IR spectra (Fig. 2c, Fig. S1). The bands at 1405 and 926 cm⁻¹ were assigned to trigonally and tetrahedrally coordinated boron respectively [29,30], making it clear that the heteroatom boron inserted into the framework of zeolites.

3.2. Catalytic performance of MWW borosilicate

The catalytic performance of the layered borosilicate zeolites in propane ODH was evaluated using a reaction gas consisting of C₃H₈, O₂ and N₂ in ratios of 1:1.5:3.5, at a total WHSV of 4.7 g/h g-cat. The propane conversions of 5.6%, 9.3% and 30.6% at about 520 °C were corresponded to BZE0-1, BZE0-2 and BZE0-3 respectively, together with the boron content increased from 1.54 wt% to 4.88 wt% (Fig. 3a). The results turned out that higher conversion was obtained at higher boron content under identical reaction condition. While BZE0-3 with more boron content exhibited higher propane conversion than BZE0-2 and BZE0-1 at same
reaction temperature, its activity degraded after long term running (Fig. 3b). The XRD pattern of the used BZEO-3 catalyst showed that the crystallinity was declined to some extent (Fig. S2). Taking into account the fact that the boron content of BZEO-3 before and after reaction remained almost identical, the deactivation process of BZEO-3 was probably caused by the declined zeolite structure. The apparent activation energies of propane over BZEO-1, BZEO-2 and BZEO-3 catalysts were of 212, 204 and 205 kJ/mol, respectively (Fig. 3c). These values were quite similar indicating that identical reaction pathway involving same active sites occurred on these catalysts. Therefore, BZEO-2 was used for further study.

Fig. 3d shows the temperature dependence of propane conversion over BZEO-2 sample. As expected, higher temperatures afford higher propane conversions. For example, as the temperature was increased from 500 to 530 °C, the propane conversion increased from 3.9% to 15.6%. The catalyst also showed good stability with both propane conversion and propylene selectivity remaining constant (−30% and −70%, respectively) for over 20 h at 540 °C (Fig. 2b). The XRD patterns of the used catalysts still retained the typical MWW structure under the ODH conditions for 20 h (Fig. S2) and the morphology of the used catalyst was almost unchanged after exposure to the reaction conditions for 20 h (Fig. S3). The major products of propane ODH consist of C3H6, C2H4, and CO, with very small amount of CO2 (<1%). The selectivity towards the desired product, propylene, decreases slightly with elevated temperatures (Fig. 3d). However, the total selectivity for light olefins (ethylene + propylene, C2-3) remained almost unchanged up to 530 °C. For example, the total selectivity to light olefins is 91.2% (propylene: 83.6%, ethylene: 7.6%) at 500 °C, and 91.6% (propylene: 80.4%, ethylene: 11.2%) at 530 °C. The selectivity of ethylene was measured to
constantly increase at elevated temperature (Fig. 2d). In the case of ethane ODH, the conversion of ethane from 3.5% increased to 37.6% when the temperature from 560 °C reached to 590 °C with the yield of ethylene from 5.1% up to 30.6% (Fig. S4). The layered borosilicate zeolite catalyze ethane ODH at a slightly higher temperature range of 560–590 °C, which is due to more energetically demanded activation of primary C–H bonds in ethane.

Moreover, the dependence of reactant partial pressure on the reaction rate was measured to investigate the kinetic behaviors (Fig. 4a, b). The kinetic analysis exhibited that the reaction order is approximately 0.5 for oxygen and a near second-order dependence of propane concentration. Similar kinetic behaviors were observed in BNOH which suggested that the BZE0-2 catalyst has an analogous reaction mechanism [15].

3.3. Identification of the possible active boron species

Benefited from the sensitivity of solid-state $^{11}$B MAS NMR spectroscopy to the local coordination environment of boron, $^{11}$B MAS and MQ MAS NMR spectra of as-prepared BZE0-2 and after different reaction intervals were measured and shown in Fig. 5 and Fig. S5. All of the one-dimensional $^{11}$B MAS NMR spectra showed broad and overlapped signals due to quadrupolar interaction. These overlapped signals can be effectively discriminated along
the F1 dimension using two-dimensional $^{11}$B MQ MAS NMR. As shown in Fig. 5a, at least five types of major B species ($B[3]^a$, $B[3]^b$, $B[3]^c$, $B[4]^a$ and $B[4]^b$) present in the catalysts. Making further efforts to obtain best fit, the one-dimensional $^{11}$B MAS NMR spectra of these catalysts acquired at magnetic fields of 11.7T and 14.1T were deconvoluted by the same parameters ($d_{iso}$, $C_Q$ and $g_Q$) guided by the sliced spectra from $^{11}$B MQ MAS NMR, and the parameters were listed in Table S2.

One-dimensional $^{11}$B MAS NMR were performed to distinguish the B species and identify the active sites. Each spectrum can be deconvoluted into five peaks with chemical shifts at ca.18, 15, 11, 0 and $-2.8$ ppm. The peaks at $-18$, $-15$ and $-11$ ppm were ascribed to tri-coordinated boron which denoted as $B[3]^a$, $B[3]^b$ and $B[3]^c$ respectively. Normally, the $^{11}$B isotropic chemical shift of trigonal boron correlates with the number of hydroxyl on B atom, and the peak at $-18$ ppm was often identified as $B(OH)_3$ [31]. Since the BZEO-2 catalyst was calcined at 550 °C, at this temperature $B(OH)_3$ is unstable due to the dehydration reaction. Thus, the $B[3]^a$ is probably corresponding to the aggregated B–O units originated from the condensation of $B–OH$. Therefore, site $B[3]^a$ was tentatively attributed to the terminal boron species $–OB–OH$ [32]. Sites $B[3]^b$ and $B[3]^c$ were assigned to framework $B(OSi)\_xOH\_{3-x}(x=1,2)$ and $B(OSi)_3$ structure [33,34]. The sharp peaks at around 0 ppm and $-2.8$ ppm were accordingly assigned to B (OH)$_3(OSi)_2$ and B(OSi)$_3$ tetrahedral framework, donated as $B[4]^a$ and $B[4]^b$ [35–37]. It can be seen that the relative amounts of boron sites in fresh and spent catalyst at 1 h TOS were similar (Fig. S5). After 20 h reaction, there was no significant change of $B[3]^c$ species, while the presence of $B[3]^a$ was increased at the cost of $B[3]^b$ species (Fig. 5c). Considering the fact that propane conversion increased from 19.9% to 29.8% during reaction period of 1 to 20 h, it can be inferred that the amount of $B[3]^a$ and $B[3]^b$ species (defective trigonal boron species) may be correlated with the catalytic activity of the catalyst in propane ODH reaction.

To further validated the assumption, the spent BZEO-2 after 20 h reaction was washed thoroughly with deionized water to remove any soluble species [38,39]. As a consequence, the boron content declined from 2.48 wt% to 0.85 wt%. In the $^{11}$B MAS NMR (Fig. 5d) spectra, the content of $B[3]^a$ and $B[3]^b$ signals decreased dramatically (by ca.72%), whereas the amount of $B[4]^a$ and $B[4]^b$ species changed marginally (Table 1). Actually, both the extra framework and incorporated boron species were removable by a washing step [31]. Therefore, it is quite difficult to distinguish which boron species belong to extra or incorporated framework only based on the results from washing experiment. The significant loss of activity by about 87% after washing implicated that there was a correlation between the amount of defective trigonal boron species and the propane conversion, i.e., in the order of blank (1.4%) < washed BZEO-2 (3.8%) < BZEO-2 after 20 h on-stream (29.8%). To elucidate the origin of active sites, we calculated the TOF of BZEO catalysts at 500 °C based on the fraction of $B[3]^a$ and $B[3]^b$ (Fig. S6, Table S3). The TOF value of BZEO-1, BZEO-2 and BZEO-3 were 4.3, 4.3 and 3.8 h$^{-1}$, respectively, indicated the intrinsic catalytic activities for the BZEO catalysts are identical under same reaction conditions. The tetrahedral boron can be transformed to trigonal structure with carefully dehydration treatment. However, the reaction conditions of ODH process was operated at ambient pressure with the presence of alkane and the
in situ formed water molecules. Besides, the relative amounts of B\(4^{+}\) in the fresh catalysts were much lower (0.2 mg\textsubscript{boron species/gcat}) compared with that of B\(3^{+}\) and B\(3^{6}\), which significantly increased to 1.88 mg\textsubscript{boron species/gcat} after 20 h running on stream. Being aware of the lack of B\(4^{+}\) in the reaction, we can conclude that the transformation of B\(4^{+}\) to B\(3^{6}\) can be ignored during the catalyst reaction. Thus, we postulate that B\(3^{+}\) and B\(3^{6}\) are responsible for the ODH activity. The results agreed well that the defective trigonal structures were the active sites, being consistent with the previous report that BO\textsubscript{3}\textsuperscript{−} rather than BO\textsubscript{4}\textsuperscript{−} species were required for propane ODH to propylene (Scheme 1) [31,40].

### 4. Conclusion

In summary, an MWW-type zeolite containing boron species was demonstrated as a promising catalyst for the ODH of propane. Structural characterization revealed that the abundance of defective trigonal boron species (B\(3^{+}\) and B\(3^{6}\)) were correlated with the activity for propane ODH. This well-defined catalyst system provided a platform for further investigation of the relationship between boron coordination environment and ODH performance.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

This study was supported by state key program of National Natural Science Foundation of China (21733302), Joint Sino-German Research Project (21761132011), Cheung Kong Scholars Programme of China (T2015036).

#### Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2020.03.021.

#### References


[2] Y. Liu, L. Luo, Y. Gao, W. Huang, CeO\textsubscript{2} morphology-dependent NbO\textsubscript{x}/CeO\textsubscript{2} interaction, structure and catalytic performance of NbO\textsubscript{x}/CeO\textsubscript{2} catalysts in oxidative dehydrogenation of propane, Appl. Catal. B 197 (2016) 214–221.


#### Table 1

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Magnetic field (T)</th>
<th>Content of boron species((\text{mg}_{\text{boron species/gcat}}))</th>
<th>Propane conversion(%)</th>
</tr>
</thead>
</table>
| in situ formed water molecules. Besides, the relative amounts of B\(4^{+}\) in the fresh catalysts were much lower (0.2 mg\textsubscript{boron species/gcat}) compared with that of B\(3^{+}\) and B\(3^{6}\), which significantly increased to 1.88 mg\textsubscript{boron species/gcat} after 20 h running on stream. Being aware of the lack of B\(4^{+}\) in the reaction, we can conclude that the transformation of B\(4^{+}\) to B\(3^{6}\) can be ignored during the catalyst reaction. Thus, we postulate that B\(3^{+}\) and B\(3^{6}\) are responsible for the ODH activity. The results agreed well that the defective trigonal structures were the active sites, being consistent with the previous report that BO\textsubscript{3}\textsuperscript{−} rather than BO\textsubscript{4}\textsuperscript{−} species were required for propane ODH to propylene (Scheme 1) [31,40].

### 4. Conclusion

In summary, an MWW-type zeolite containing boron species was demonstrated as a promising catalyst for the ODH of propane. Structural characterization revealed that the abundance of defective trigonal boron species (B\(3^{+}\) and B\(3^{6}\)) were correlated with the activity for propane ODH. This well-defined catalyst system provided a platform for further investigation of the relationship between boron coordination environment and ODH performance.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

This study was supported by state key program of National Natural Science Foundation of China (21733302), Joint Sino-German Research Project (21761132011), Cheung Kong Scholars Programme of China (T2015036).


Formation of supported rhodium clusters from mononuclear rhodium complexes controlled by the support and ligands on rhodium, Phys. Chem. Chem. Phys. 16 (2014) 1262–1270.


