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# COMMUNICATION

# Boron-hyperdoped Silicon for the Selective Oxidative Dehydrogenation of Propane to Propylene

Received 00th January 20xx, Accepted 00th January 20xx Junjie Chen<sup>a</sup>, Parham Rohani<sup>a</sup>, Stavros G. Karakalos<sup>b</sup>, Michael J. Lance<sup>b,†</sup>, Todd J. Toops<sup>c,†</sup>, Mark T. Swihart<sup>a</sup>, Eleni A. Kyriakidou<sup>a,</sup>\*

DOI: 10.1039/x0xx00000x

Boron containing catalysts have great potential in the oxidative dehydrogenation of propane reaction. Herein, a series of 15, 25 and 42 at.% boron-hyperdoped silicon catalysts synthesized by laser pyrolysis were studied. Boron-hyperdoped silicon samples showed >6 times higher propylene productivity than commercial h-BN at 450 °C.

Propylene ( $C_3H_6$ ) is one of the most important building blocks in the petrochemical industry. It is used in the production of many industrial products, such as polypropylene, propylene oxide and isopropanol.<sup>1</sup> Propylene is traditionally produced by steam cracking and fluid catalytic cracking in petroleum refineries. However, both technologies have low selectivity, high energy consumption and significant production of  $CO_2$  emissions.<sup>2,3</sup> Direct production of  $C_3H_6$  by the dehydrogenation of propane ( $C_3H_8$ ) is currently of great interest in an effort to close the  $C_3H_6$ supply and demand gap in the US.<sup>4</sup> The oxidative dehydrogenation of propane (ODHP) reactions have attracted extensive attention as they are more resistant to coke deposition compared to the non-oxidative DHP reactions and they are not limited by equilibrium.<sup>5,6</sup>

Various supported metal oxide catalysts have been studied for the ODHP reaction, such as vanadium,<sup>7-14</sup> molybdenum<sup>15-18</sup>

and chromium oxides<sup>19-23</sup>. However, most metal oxide catalysts have low  $C_3H_6$  selectivities (<60%), very low  $C_3H_6$  productivities (<1  $g_{C_3H_6}g_{cat}^{-1}h^{-1}$ ) and form significant amounts of over-oxidation byproducts (CO and CO<sub>2</sub>; 20-50% CO<sub>x</sub> selectivity).<sup>4,12,24,25</sup> Recently, Hermans et al. reported that commercial hexagonal boron nitride (h-BN) provides excellent selectivity towards propylene (79%) and ethane (12%) with negligible  $CO_x$  ( $\leq$ 5%) formation.<sup>26</sup> However, h-BN had a C<sub>3</sub>H<sub>6</sub> productivity of as low as 0.82  $g_{C_{3}H_{6}}g_{cat}$ -<sup>1</sup>h-<sup>1</sup> and required surface activation (oxidation and hydrolyzation) to obtain its reported activity.<sup>27</sup> More recently, Lu et al. showed that commercial silicon boride had a promising ethylene, propylene and isobutylene productivity  $(1.2^{2.6} g_{olefins} g_{cat}^{-1} h^{-1})$  towards the oxidative dehydrogenation of light alkanes.<sup>28</sup> Furthermore, mesoporous silica-supported boron oxide catalysts (SOB-10) showed a C<sub>3</sub>H<sub>6</sub> productivity of 2.06  $g_{C_{3}H_{6}}g_{cat}{}^{-1}h^{-1}$  at 500  $^{o}C.^{29}$  Tri-coordinated boroxol and hydroxylated linear boron species were reported to be the active sites for ODH based on Density Functional Theory (DFT) calculations.

Herein, a series of boron-hyperdoped silicon catalysts were synthesized by a laser pyrolysis process, with boron concentrations of 15, 25 and 42 at.% that were reported to be stable up to annealing temperature of 600 °C.<sup>30</sup> Unlike traditional doping methods, where the dopant concentration is limited by its solid solubility, hyperdoping allows boron doping on silicon to exceed the solubility of boron (1.2 at.%) resulting to high boron concentrations. This synthesis method facilitated the formation of boron enriched surface active sites that contribute to excellent  $C_3H_6$  productivity under ODHP reaction conditions. Fourier-transform infrared spectroscopy and B1s XPS spectra indicated the presence of BO<sub>x</sub> and B-OH species in boron-hyperdoped silicon samples that can serve as the active sites for ODHP.

The morphology and composition of the synthesized boronhyperdoped silicon catalysts synthesized by the laser pyrolysis method were determined by TEM and EDS mapping (Fig. 1). Fig. 1a-d shows that as-prepared pure silicon and boronhyperdoped silicon catalysts containing 15, 25 and 42 at.%

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<sup>&</sup>lt;sup>+</sup> This manuscript has been co-authored by UT-Battelle, LLC, under Contract No. DE-AC05000R22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for the United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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**Fig. 1.** TEM images of (a) pure silicon and (b) 15 at.%, (c) 25 at.% (d) 42 at.% boron-hyperdoped silicon catalysts, (e) HAADF-TEM and EDS mapping of (f) B, (g) Si and (h) O of 42 at.% boron-hyperdoped silicon catalysts.

boron had a spherical shape with an average size of around 34.5, 18.6, 19.1 and 18.9 nm (Fig. S1), respectively. Fig. 1a-d shows that boron-hyperdoped silicon catalysts were partially aggregated, attributed to the rapid heating and cooling during the laser pyrolysis synthesis.<sup>30</sup> EDS mapping of 42 at.% boronhyperdoped silicon (Fig. 1e-h) showed that use of the laser pyrolysis synthesis method can lead to homogeneously dispersed B and Si over the catalyst. Furthermore, a layer of O can be observed on the surface of 42 at.% boron-hyperdoped silicon particles (Fig. 1h). The BET surface areas and BJH pore volumes of pure silicon and boron-hyperdoped silicon measured by  $N_2$  physisorption are shown in Table S1.  $N_2$ adsorption and desorption isotherms are shown in Fig. S2. All samples synthesized by laser pyrolysis had similar surface areas  $(89 - 101 \text{ m}^2/\text{g})$  and pore volumes  $(0.36-0.41 \text{ cm}^3/\text{g})$ , indicating that they have similar structures. The theoretical surface area of boron-hyperdoped silicon was calculated to be  $\sim 80 \text{ m}^2/\text{g}$  by assuming that the catalyst has a monodispersed spherical shape and taking into account that boron and silicon have similar densities (B density: 2.34 g/cm<sup>3</sup>; Si density: 2.53 g/cm<sup>3</sup>).<sup>31,32</sup> This close approximation of the theoretical and experimental surface areas (Table S1), suggests that the catalysts are mainly non-porous with their pore volume attributed to the gaps between the aggregated particles.<sup>33</sup>

The performance of pure silicon and boron-hyperdoped silicon catalysts containing 15, 25 and 42 at.% boron towards the ODHP reaction was evaluated and the results are shown in Fig. S3 and Fig. 2(a-c). Pure silicon nanoparticles showed negligible  $C_3H_8$  conversions (< 0.15%) and high  $CO_2$  selectivities (>40%) at temperatures ranging from 420 to 450 °C. The low reactivity of pure silicon indicated that it was inert towards the ODHP reaction; in fact, the reactivity is on par with reported homogeneous gas phase reactions.<sup>34</sup> The performance of silicon nanoparticles was significantly improved when doped with boron. Specifically, 15 at.% boron-hyperdoped silicon showed an increase in  $C_3H_8$  conversion from 0.12 to 5.2% compared to pure silicon at 450 °C (Fig. 2a, Table S2). Moreover, 15 at.% boron-hyperdoped silicon sample showed an increase in  $C_3H_6$  selectivity to > 60% and a decrease in  $CO_x$ formation to <5%, indicating that boron hyperdoping generated active sites on the silicon surface for the ODHP reaction. Small amounts of  $C_2H_4$  ( $S_{C_2H_4}$  = 6.2%) were also observed over 15 at.%

boron-hyperdoped silicon at 450 °C due to C-C bond cleavage. Increasing the boron concentration from 95 to 259 at % 90 refer enhanced the ODHP activity (Fig. 2b). Specifically, >70% alkene selectivity was achieved ( $S_{C_3H_6} = 64.1 \%$ ,  $S_{C_2H_4} \sim 7.2\%$ ) over 25 at.% boron-hyperdoped silicon (Table S2). The C<sub>3</sub>H<sub>8</sub> conversion of 25 at.% boron-hyperdoped silicon (10.6 %) was 2 times higher than that of 15 at.% boron-hyperdoped silicon (5.2%) at 450 °C. We attribute this increase to boron enrichment of the active sites achieved with increased boron concentration. However, 42 at.% boron-hyperdoped silicon sample showed a decreased activity ( $X_{C_{aH_a}}$  = 5% at 450 °C), which can be attributed to boron leaching out from the silicon lattice. All boron-hyperdoped silicon samples showed a similar product distribution, with alkane selectivity slightly increasing and CO<sub>x</sub> selectivity decreasing with increasing boron concentration from 15 to 42 at.%. Apart from alkene formation (C<sub>3</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>), C1 products such as HCHO, CH<sub>3</sub>OH and HCOOH were produced through a gas phase radical reactions in which CH3• intermediate can be generated from C-C bond cleavage.<sup>35,36</sup> Commercial h-BN (9.1 m<sup>2</sup>/g) (Fig. S4), porous BN (43.8 m<sup>2</sup>/g) (Fig. S5), and 21.7 wt.% B/SiO<sub>2</sub> (Fig. S6) were also evaluated under the same reaction conditions as the boron-hyperdoped silicon catalysts. Commercial h-BN catalyst had a 7-15 times lower C<sub>3</sub>H<sub>8</sub> conversion (0.7%) at 450 °C compared to boron-hyperdoped silicon samples. The C<sub>3</sub>H<sub>6</sub> selectivity of commercial h-BN was 83.6% with 4% CO formation and negligible CO<sub>2</sub> formation. Porous BN showed slightly higher C<sub>3</sub>H<sub>8</sub> conversion (1%) than h-BN (0.7%). The benefit of the hyperdoping method compared to convention impregnation methods is illustrated by comparing the performance of 21.7 wt.% B/SiO<sub>2</sub> synthesized by wet impregnation with 42 at.% boron-hyperdoped silicon. The 21.7 wt.% B/SiO<sub>2</sub> and 42 at.% boron-hyperdoped silicon catalysts have the same weight of B. The C<sub>3</sub>H<sub>8</sub> conversion achieved by 42 at.% boron-hyperdoped silicon at 450 °C (5%) was 10 times higher than that of 21.7% B/SiO<sub>2</sub> (0.5%). This phenomenon can be attributed to the well dispersed boron containing sites (Fig. 1f) achieved by the hyperdoping method. It is worth noting that porous BN, 21.7 wt.%  $B/SiO_2$  and h-BN have similar product distributions and C<sub>3</sub>H<sub>6</sub> selectivity (~80%), indicating a similarity in active sites. The apparent activation energies of boron-hyperdoped silicon, h-BN, porous BN, and 21.7 wt.% B/SiO<sub>2</sub> samples are shown in Fig. 2d and Table S3. The apparent activation energies of 15, 25 and 42 at.% boronhyperdoped silicon samples were similar (148.6-160.5 kJ/mol) and they were lower than the apparent activation energies of h-BN, porous BN, and 21.7 wt.% B/SiO<sub>2</sub> (180.0-188.3 kJ/mol). A comparison of reaction rates at 450 °C is shown in Fig. 2e. The reaction rates of boron-hyperdoped silicon samples outperformed all other studied samples in the following order: 25 at.% > 15 at.% = 42 at.% boron hyperdoped silicon > porous BN > h-BN > 21.7 wt.%  $B/SiO_2 > pure silicon$ . The lower apparent activation energies and the higher reaction rates of boronhyperdoped silicon compared to porous BN, h-BN and B/SiO<sub>2</sub> catalysts can be attributed to the enriched surface active sites and potential lower contribution of gas phase reactions over the boron-hyperdoped silicon samples. The catalytic stability at 450 °C of all studied samples is shown in Fig. 2f. Except from the 25

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**Fig. 2.**  $C_3H_8$  conversion and product selectivity as a function of reaction temperature over (a) 15 at.%, (b) 25 at.% and (c) 42 at.% boron-hyperdoped silicon catalysts; (d) apparent activation energies, (e) reaction rates at 450 °C and (f) stability tests at 450 °C of 15, 25, 42 at.% boron-hyperdoped silicon, commercial h-BN, porous BN, 21.7 wt.% B/SiO<sub>2</sub> and pure silicon samples ( $C_3H_8:O_2:Ar = 1:1.5:3.5$ , WHSV = 28.2  $g_{C_3H_8}g_{cat}$ <sup>-1</sup> h<sup>-1</sup>).

at.% boron-hyperdoped silicon sample, all other studied catalysts showed stable performance at 450 °C. During the stability test, the  $C_3H_6$  productivity over pure silicon was negligible (0.01  $g_{C_3H_6}g_{cat}$ <sup>-1</sup>h<sup>-1</sup>), while commercial h-BN had a productivity of 0.16  $g_{C_3H_6}g_{cat}$ <sup>-1</sup>h<sup>-1</sup>. Porous BN showed a better productivity (0.21  $g_{C_3H_6}g_{cat}$ <sup>-1</sup>h<sup>-1</sup>) than h-BN. The boron-hyperdoped silicon samples had 5 times higher  $C_3H_6$  productivity compared to h-BN. 15, 42 at.% boron-hyperdoped silicon samples showed stable  $C_3H_6$  productivities at 450 °C. However, a continuous decrease in  $C_3H_6$  productivity was observed over 25 at.% boron-hyperdoped silicon sample.

To gain a better understanding of the origin of the catalyst activity, FTIR (Fig. 3a) and XPS (Fig. 3b, Fig. S7, 8) spectra of fresh pure silicon, 15, 25 and 42 at.% boron-hyperdoped silicon samples were collected. In the FTIR spectra (Fig. 3a), the peaks at ~999, 1127 cm<sup>-1</sup> in the quartz sand spectrum and the peaks at 1100-1200 cm<sup>-1</sup> in the pure silicon spectrum are attributed to Si-O-Si asymmetrical stretching modes.<sup>37</sup> New peaks can be observed over boron-hyperdoped silicon samples. The peaks at ~1200 and 1416 cm<sup>-1</sup> can be attributed to B-O bonds and the peak at around 3227 cm<sup>-1</sup> is attributed to B-OH.<sup>30</sup> Both B-O and B-OH are regarded as active species for ODHP reactions.<sup>29</sup> Moreover, the peak intensity of B-O and B-OH increased with increasing boron concentration. Neither B-O nor B-OH peaks were observed over pure silicon or quartz sand, which is consistent with their inert nature towards ODHP reaction. XPS further confirms the present of B<sub>x</sub>O<sub>y</sub> species (~193.5 eV, Fig. 3b), SiO<sub>2</sub> (~103.2 eV) and SiO (~101.2 eV) (Fig. S8) on the surface of boron-hyperdoped silicon samples. 33,38 About 30% of surface boron was present as  $B_xO_y$  species and the rest was present as SiB (~187.9 eV). The surface B/(Si+B) ratio also increased from



**Fig. 3.** (a) FTIR spectra of quartz sand, pure silicon, 15, 25 and 42 at.% boron-hyperdoped silicon samples, (b) B1s XPS spectra of 15, 25, and 42 at.% boron-hyperdoped silicon samples ( $B_xO_y$  and SiB peak ratios are as marked).

33.3 to 42.8% with an increase in B doping concentration from 15 to 25 at.% (Table S4). This observation is consistent with the improved ODHP performance with increasing boron loading (Fig. 2a-b). Increasing the boron doping concentration even further from 25 to 42% led to an increase in surface B/(Si+B) ratio from 42.8% to 47.8%. However, the increase in surface B/(Si+B) ratio with increasing boron loading from 25 to 42 at.% led to a decrease in ODHP performance. This observation requires further investigation.

Table S2 summarizes the performance of the studied ODHP catalysts and the ones reported in literature. Fig. S9 shows a comparison of the  $C_3H_6$  productivity of the boron-hyperdoped silicon catalysts and other reported ODHP catalysts. A comparison of  $C_3H_6$  conversion and  $C_3H_6$  selectivity is shown in Fig. S10. Boron-hyperdoped silicon catalysts showed higher

C<sub>3</sub>H<sub>6</sub> productivity compared to other metal oxide catalysts, e.g. Cr<sub>2</sub>O<sub>3</sub>/SBA-15, F-V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>, even at relative low reaction temperatures (400-450 °C). As one of the most well-studied catalysts for ODHP reactions, V<sub>2</sub>O<sub>5</sub>/SBA-15 had slightly higher C<sub>3</sub>H<sub>6</sub> productivity than that of the boron-hyperdoped silicon samples, but required a much higher reaction temperature (550 °C). Moreover, V<sub>2</sub>O<sub>5</sub>/SBA-15 had a significantly higher CO<sub>2</sub> selectivity (25.2% at 550 °C) compared to 25 at.% boronhyperdoped silicon (S<sub>CO2</sub> = 2.5% at 450 °C).

In summary, we reported a new type of ODHP catalyst: boron-hyperdoped silicon with varied boron concentration (0 -42 at.%) which was synthesized by laser pyrolysis and showed excellent  $C_3H_6$  productivity. The boron-hyperdoped silicon had a  $C_3H_6$  productivity of > 0.94  $g_{C_3H_6}g_{cat}$ <sup>-1</sup>h<sup>-1</sup> at 450 °C, which is >6 times higher than the  $C_3H_6$  productivity of commercial h-BN catalyst (0.16  $g_{C_3H_6}g_{cat}$ <sup>-1</sup>h<sup>-1</sup>) under the same reaction conditions. Boron doping above the solubility limit of boron in silicon can be achieved by the laser pyrolysis synthesis method, enabling the formation of enriched surface BO<sub>x</sub> and B-OH active sites. Comparing to commercial h-BN and porous BN, boronhyperdoped silicon catalysts showed lower apparent activation energies and significantly higher reaction rates at 450 °C.

Access to the FEI Talos F200X STEM was provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program and the Nuclear Science Facilities. This research was sponsored by start-up funding from the UB Department of Chemical and Biological Engineering and the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy. A portion of this research was also sponsored by the Vehicle Technologies Office at the U. S. Department of Energy.

## **Conflicts of interest**

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There are no conflicts to declare.

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