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Selective Oxidative Cracking of *n*-Butane to Light Olefins over Hexagonal Boron Nitride with Limited Formation of CO_x

William P. McDermott^[a], Juan Venegas^[b], and Ive Hermans*^[a,b]

Abstract: In recent years, hexagonal boron nitride (hBN) emerged as an unexpected catalyst for the oxidative dehydrogenation (ODH) of alkanes. Here, we extend the versatility of hBN to alkane oxidative cracking chemistry by investigating the production of ethylene and propylene from *n*-butane. Cracking selectivity is primarily controlled by the ratio of *n*-butane to O₂ within the reactant feed. Under O₂-lean conditions, increasing temperature leads to increased selectivity to ethylene and propylene and decreased selectivity to CO_x. In addition to surface-mediated chemistry, homogeneous gas-phase reactions likely contribute to the observed product distribution and a reaction mechanism is proposed based upon our observations. The catalyst shows good stability under oxidative cracking conditions for 100 hr time-on-stream while maintaining high selectivity to ethylene and propylene.

Introduction

Light olefins such as ethylene and propylene are two of the most vital building blocks in the chemical industry as they are the starting point for many (co-)polymers, oxygenates, and other bulk chemicals. In 2017, the global market for ethylene and propylene stood at 170 Mt and 130 Mt, respectively.^[1] Historically, the majority of light olefins have been produced through steam cracking of petroleum-derived naphtha.^[2] Despite the emergence of light olefin production through fluid catalytic cracking (FCC) or direct methods like propane dehydrogenation (PDH), steam cracking remains the "workhorse" light olefin production technology.^[2-4] Steam cracker furnaces are typically operated in the temperature range of 850–900°C to provide the energy for the pyrolysis of naphtha into lighter molecules. These operating conditions result in process emissions of approximately 1.8-2.0 t CO₂/t ethylene from fuel consumption.^[5] Moreover, high reaction temperatures lead to coke deposition within the reactors which must be periodically removed leading to significant reactor downtimes. For these reasons, the development of processes that require less energy and do not produce coke deposits could lead to significant cost-savings in the production of light olefins and is of interest to academic and industrial researchers.

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The oxidative cracking of higher hydrocarbons to light olefins has the potential to be economically competitive with steam cracking.^[6] The exothermic oxidative reaction lends itself to lower reaction temperatures than the endothermic nonoxidative steam cracking. The heat generated during oxidative cracking may even enable autothermal reactor operation, reducing heat input during operation and thus decreasing fuel consumption.^[7,8] The incorporation of O₂ within the feed also prevents the fast build-up of coke deposition.

Many catalysts have been studied for the oxidative cracking of hydrocarbons to light olefins such as Li-doped metal oxides,^[9–12] metal oxychlorides,^[13] noble metal-coated monoliths,^[7,8,14–16] supported Co catalysts,^[17–19] and supported Au catalysts.^[20–22] Many of these systems have substantial disadvantages, such as poor catalyst stability or reaction conditions not largely different from those employed in nonoxidative cracking. The most significant drawback shared by all oxidative cracking catalysts explored thus far has been the significant co-production of CO₂, which has been identified as main bottleneck in achieving success in oxidative cracking technology.^[6]

Leveles et al. investigated the kinetics and mechanism of the oxidative cracking of propane over a Li/MgO catalyst.^[10] They reported that the reactive oxygen species on the catalyst surface enable the energetically-preferred secondary H-abstraction from propane to form *i*-propyl radical and under nonoxidative conditions, this radical can undergo unimolecular C-C cleavage to form ethylene and CH₃•. The CH₃• radical acts as a radical chain carrier and abstract H atoms from propane and form *i*-propyl and *n*-propyl radicals. The *n*-propyl radical can decompose into propylene and H \bullet . Under oxidative conditions, the role of O₂ is two-fold. Beyond regenerating the active sites, the presence of O₂ changes the radical pool in the gas phase. The reaction of O₂ with propyl radicals forms propylene and HOO. H-abstraction by HOO• from propane leads to propyl radicals and H₂O₂. The decomposition of H₂O₂ to HO• (chain initiation) adds to the pool of gas phase radical chain carriers. The production of CO and CO2 (CO_x) mainly occurred through overoxidation pathways on the surface of the catalyst.

In recent years, our group has shown that hexagonal boron nitride (hBN), boron nitride nanotubes (BNNTs), and other boroncontaining catalysts exhibit high selectivity in the oxidative dehydrogenation (ODH) of propane, *n*-butane, and isobutane^[23–25] In these studies, a variety of spectroscopic techniques such as XPS, Raman, and IR revealed that after exposure to reaction conditions, these boron-containing materials become functionalized with oxygen at their surface. We recently employed solid-state NMR to investigate boron nitride materials and demonstrated that the oxidized phase on used boron nitride catalysts can be denoted as B(OH)_xO_{3-x} (0≤x<2), which contains the active site for ODH.^[26] During reaction kinetic studies of hBN-

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catalyzed ODH, it was revealed that the O₂ partial pressure (P_{O2}) greatly influenced the observed product distribution.^[24] Performing the oxidation of *n*-butane at dilute P_{O2} results in a product distribution that consists mainly of cracking products (*i.e.* ethylene, propylene). Increasing P_{O2} resulted in increased selectivity to the primary ODH products, 1-butene, *cis*-2-butene and *trans*-2-butene.

Thus far, reports from our group and others have primarily discussed the role of the surface of hBN in the mechanism of alkane ODH.[23,24,27-29] These contributions demonstrated the importance of O2 activation on the hBN surface and that the resulting reactive surface oxygen species likely initiate dehydrogenation through H-abstraction from the gas phase alkane. In a recent report evaluating mass and heat transfer phenomena in the hBN-catalyzed ODH of propane,^[30] we found that increasing catalyst dilution led to a significant increase in the rate of alkane consumption at a constant mass of catalyst, indicating that reactions in the gas phase contribute substantially to the reactivity of boron-containing catalysts. As our findings are not consistent with a reaction in which the surface is mainly responsible for catalytic activity, we put forward the hypothesis that the oxidation of alkanes over hBN proceeds through a surface-initiated radical propagation reaction. This hypothesis is plausible given the evidence for such a mechanism has been put forward for other catalyst systems such as Li/MgO.

In this contribution, we investigate hBN for the oxidation of nbutane to produce ethylene and propylene. We have chosen nbutane to serve as a model hydrocarbon substrate in these studies so that the experimental results can inform the future investigation of more complex hydrocarbon feeds. Our main objective in this study is to probe the role of various reaction parameters such as reactant partial pressures and temperature and their effect on activity and product distribution. We also demonstrate that hBN does not exhibit any deactivation over the course of 100 hr time-on-stream (TOS) despite low O2 availability to oxidize potential coke deposits. By altering Po2 and observing how the rate of formation of each product evolves, we show that the mechanism of oxidative cracking over hBN is likely similar to that of a previously studied cracking catalyst which can be attributed to homogeneous gas-phase chemistry present in these systems. By comparison, hBN produces less COx, especially CO2.

Results and Discussion

Fresh hBN exhibits an induction period attributed to the oxidation of surface boron species.^[31] Prior to O₂-lean oxidative cracking experiments, fresh hBN was activated under an O₂-rich feed of 0.20 atm *n*-C₄H₁₀, 0.10 atm O₂, and 0.70 atm N₂ for 24 hr at 550 °C. Figure S1 demonstrates the growth of the reactivity of hBN with time on stream, with *n*-butane conversion ($X_{n-C4H10}$) 23.7% before decreasing mildly and reaching a steady state value of 20.3%.

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Figure 1. (a) Conversion of reactants in the oxidative cracking of *n*-butane as a function of reaction temperature. (b) Rate of formation of products as a function of reaction temperature. Balance gas is N₂ to a P_{tot} of 1 atm.

After catalyst pre-treatment, we initially sought to determine if the selectivity trends observed at low P_{O2} held at higher $X_{n-C4H10}$. Our initial oxidative cracking experiments were performed mostly in the differential regime ($X_{n-C4H10} < 10\%$) to obtain valuable kinetic data.^[24] Because of the apparent O₂ adsorption dependence, it is understood that O₂-lean feeds lower alkane consumption levels. To overcome lower alkane conversions observed under O2-lean conditions, we employ reaction temperatures higher than those typically employed for hBN-catalyzed n-butane ODH under O2rich conditions. A range of temperatures were scanned at a Pn-C4H10: PO2 ratio of 16 and an inverse weight-hourly-space-velocity (WHSV⁻¹) of 27.5 kg_{cat} s mol_{n-C4H10}⁻¹. As temperature increases from 475°C to 575°C, Xn-C4H10 increases linearly from 4.3% to 19.8% while X₀₂ increases from 36.2% to 76.6% where it begins to level off (Figure 1a). The rate of C4 olefin production increases slightly at 500° but then begins to decrease with increasing

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550°C. Reaction conditions are further tabulated in Table S1.

temperature (Figure 1b). In this temperature range, the rates of methane and propylene increase and maintain close to a 1:1 ratio, suggesting that they arise from the same C₄ intermediate that decomposes into C₃ and C₁ fragments. The rate of ethylene formation ethylene is significantly higher than that of ethane, suggesting that under these conditions, the cracking of *n*-butane into C₂ fragments results in primarily ethylene. The production of CO_x only shows slight increases.

Under O₂-lean conditions, the substantial difference between the rates of formation of cracking products and C₄ with increasing temperature has a significant impact on selectivity. Over the temperature range examined, selectivity to ethylene and propylene increases from 18.5% to 24.5% and from 25.4% to 45.2%, respectively (Figure S2). As the rate of cracking product formation outpaced that of C4 olefins, the combined selectivity to C4 olefins (1-butene, trans-2-butene, cis-2-butene, isobutene, and 1,3-butadiene) decreases substantially from 45.7% to 7.8%. The increase in reaction temperature also decreases CO_x selectivity, which remained under 2%. This change in selectivity is not solely conversion-dependent as the product distribution at isoconversion is significantly shifted toward cracking products at higher temperature (Figure S3). We originally reported that under O2-rich conditions at lower temperatures the product selectivity in the oxidation of *n*-butane was independent of temperature in the range of 440 - 480 °C.^[24] The reaction conditions employed here contribute to temperature-dependent reactivity trends.

Indeed, the results under O₂-lean conditions contrast with those obtained under O₂-rich conditions. With a $P_{n-C4H10}$: P_{O2} of 2:1 and the previously employed *WHSV*⁻¹ of 27.5 kg_{cat} s mol_{*n*-C4H10}⁻¹, C₄ olefin production increases linearly with temperature from 475°C until 575°C where the rate begins to decrease. Over this range, the rate of formation of cracking product increases and the production of CO follows the same trend. Therefore, enhanced selectivity to cracking products can be obtained at high

temperatures under O_2 -rich conditions but with undesirable CO_x formation. (Figure S4).

The influence of contact time was investigated at a $P_{n-C4H10}$: P_{O2} of 16 at a temperature of 550°C. Although $X_{n-C4H10}$ increases from 7.8% to 17.2% as *WHSV*⁻¹ increases from 15.7 to 55.0 kg_{cat} s mol_{*n*-C4H10}⁻¹ (Figure S5), the product selectivity is not altered significantly. Thus, temperature and contact time can be increased to overcome lower alkane conversions under O₂-lean conditions.

We then examined the influence of $P_{n-C4H10}$: P_{O2} on the product distribution to see if the trends observed at low alkane conversion are consistent with those at elevated conversion (Figure 2). For a valuable comparison, selectivity data were obtained at isoconversion by altering the feed conditions to the desired partial pressures and adjustment of contact time. As the ratio is increases, the selectivity to propylene and methane increase while ethylene remains relatively constant. Additionally, the selectivity to ethane becomes significant, suggesting the production of ethane is directly related to the O2 content in the feed. Most importantly, the selectivity to COx decreases with increasing *P*_{n-C4H10}:*P*_{O2}. As oxidative cracking over hBN is affected by P_{O2} , we hypothesized that the undesirable selectivity to CO_x from previously studied catalysts may have stemmed from nonoptimal reaction conditions. Many of the catalysts in the literature are tested under O₂-rich feed ($P_{n-C4H10}$: $P_{O2} < 1$) and it is unclear how these catalysts would perform under a more optimized set of reaction conditions. Therefore, we synthesized an $Li_2O/Dy_2O_3/MgO$ catalyst based upon a literature procedure $^{\left[9\right]}$ with a nominal loading of 7.7% Li₂O and 7.3% Dy_2O_3 and evaluated it under O₂-lean conditions. Investigating this catalyst at P_{n-C4H10}:P_{O2} of 16, we observed over a 30-fold increase in the CO₂ selectivity at comparable $X_{n-C4H10}$ relative to hBN. This difference suggests that low COx selectivity is inherent to hBN and not only a consequence of decreased O2 availability in the feed. Apart from COx selectivity, the pattern in selectivity between hBN and Li₂O/Dy₂O₃/MgO under O₂-lean conditions is nearly identical. This similarity suggests that there exist commonalities in the

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mechanism of oxidative cracking between these materials, which we hypothesize to be the result of similar gas phase contributions in their mechanism.



Figure 3. Rate of product formation in the oxidation of *n*-butane over hBN as a function of the partial pressure of O₂. $X_{n-C4H10} = 0.5 - 5.1\%$. Balance gas is N₂ to a P_{tot} of 1 atm.

In order to gain further insight into the reaction mechanism in hBN-catalyzed oxidative cracking, we investigated the rate of formation of each product at varying P_{02} while maintaining constant *n*-butane contact time and ensuring that the reaction is under differential conditions ($X_{n-C4H10} < 10\%$). Under nonoxidative conditions ($P_{02} = 0$), only cracking products are observed, *i.e.* methane, ethane, ethylene and propylene (Figure 3), consistent with unimolecular decomposition of radicals in the gas phase. Only trace amounts of C₄ olefins were detected, suggesting that O₂ is essential for the production of ODH products under these reaction conditions. The rate of formation of C₄ olefins increases sharply with increasing P_{02} over the entire range investigated. The rate of formation of methane decreases with a concurrent increase in the rate of formation of CO. This relationship suggests that CH₃• species formed during cracking can abstract H• from another gas phase species to form methane or be oxidized to CO in the presence of O2. The rate of formation of ethylene and propylene reach their maximum at approximately $P_{O2} = 0.02$ atm. Above this point, any increases in Po2 only influences the production of ODH and COx products.

To provide more insight into the formation of butenes in the oxidative cracking of *n*-butane, the rate of formation of each C₄ olefin in addition to the ratio of 1-butene:2-butenes was investigated as a function of P_{O2} (Figure S6). The ratio of butene isomers, 1-butene:*trans*-2-butene:*cis*-2-butene, gives information on the nature of the second H-abstraction. A statistical distribution, 3:1:1, implies that the second H-abstraction to form the olefin is entropically controlled and a thermodynamic distribution, 1:1:1, implies that it is energetically controlled.^[32,33] In our experiment, the ratio 1-butene:2-butenes falls between 1.14–1.23, close to our

previously reported value of approximately 1.3–1.4 under slightly different reaction conditions.^[24] These values are closer to a statistical distribution, signifying that the second H-abstraction is most likely entropically controlled. As the formation of C₄ olefins increases substantially with P_{O2} , we believe that the second H-abstraction is performed in the gas phase with very reactive abstracting agents with no energetic preference for primary or secondary H atoms, hence why we observe a statistical distribution.



Figure 4. Proposed gas phase mechanism in the oxidation of *n*-butane over hBN. The reactions are numbered in black or red for pathways not dependent or dependent on gas phase O₂, respectively (see text).

Similarities in the product distribution between hBN and $Li_2O/Dy_2O_3/MgO$ (*vide supra*) led us to investigate the influence of P_{O2} in the rate of formation of products in the latter system. This study reveals highly similar trends in the rate of product formation under differential conditions (Figure S7) between these catalysts. The most significant difference is that the production of CO_2 is more substantial over $Li_2O/Dy_2O_3/MgO$ than it is with hBN. These similar trends in product formation rates allow us to surmise that the cracking of alkanes over these materials have closely related mechanisms. As the surfaces of these materials are presumably quite different in nature, identical gas phase reactions occurring in both systems could explain the analogies in product distributions.

Figure 4 presents a gas phase reaction network that accounts for our experimental observations. The fate of the radical species formed during the reaction depends on the presence of O₂. The pathways independent of O₂ (numbered in black in Figure 4) predominate under O₂ starvation conditions. Regardless of P_{O2} , we propose that the reactive B-O moieties on the surface abstract the energetically-preferred secondary H-atom to form secondary *n*-butyl radicals (1). Under O₂-lean conditions, the majority of these radicals will decompose to form propylene and CH₃• (2), according to the β -scission rule.^[34] CH₃• acts as a chain carrier which will form CH₄ upon H• abstraction from *n*-butane to form primary and secondary *n*-butyl radicals (3).^[35] Primary radicals

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undergo β -scission to form ethyl radical and ethylene (4). The ethyl radical forms ethane upon H abstraction of *n*-butane (5) or can eject H• to form ethylene (6), the latter reaction providing the reasoning for ethylene comprising the large majority of the C₂ selectivity under all tested conditions.^[36]

With addition of O2, new reaction pathways are accessible (numbered in red in Figure 4). The reaction of alkyl radicals with O2 to form alkylperoxy adducts is well established in the literature.[37-39] The decomposition of these adducts result in the formation of an olefin and HOO. Thus, reaction of secondary nbutyl radicals formed at the catalyst surface with O2 forms 1butene, trans-2-butene, and cis-2-butene (7). The HOO• radical, like CH₃•, will further react with *n*-butane molecules to form additional alkyl radicals (4). The H₂O₂ formed in this step generates two HO• radicals upon decomposition (8); this HO• radical becomes the main chain carrier under oxidative conditions.^[10] In addition to the nonoxidative processes described above, the primary radical can react with O_2 to form 1-butene (9). The presence of O₂ also affects the fate of the alkyl radicals formed from C-C cleavage. CH3• can oxidize to COx (10) and ethyl radical forms ethylene upon H-abstraction (11), explaining the loss of ethane production with increasing P_{02} . Further studies are required to fully characterize radical species present in high temperature hydrocarbon oxidations. Recently, Luo and coworkers employed a synchrotron VUV photoionization mass spectrometry (SVUV-PIMS) technique that allowed for the detection and characterization of radical species present in the oxidation of methane and ethane over Li/MgO.^[40] Species analogous to those proposed here such as alkylperoxy radicals were detected and this may prove to be a valuable technique in the study of oxidative cracking mechanisms.



Figure 5. Conversion and selectivity of the oxidative cracking of *n*-butane over hBN as a function of time-on-stream. $P_{n-C4H10} = 0.20$ atm, $P_{02} = 0.0125$ atm, balance gas is N₂ to a P_{tot} of 1 atm. T = 550 °C, *WHSV*⁻¹ = 55.0 kg_{cat} s mol_{*n*-C4H10}⁻¹. Conversion and selectivity labels reflect their value when the experiment was discontinued.

Catalyst stability is an important concern when considering a new catalyst for oxidative cracking. Nonoxidative cracking catalysts

suffer from deactivation due to coke deposition and oxidative cracking catalysts deactivate from degradation of the active phase through evaporation or phase change. hBN has been shown to be highly stable for up to 300 hr in the ODH of ethane at 530°C.^[41] Since O₂-lean feeds are being used here to favor selectivity to light olefins, coke deposition may play a more significant role as O₂ availability to oxidize carbon species is decreased. After the initial O2-rich treatment of hBN described above, the stability of hBN was investigated for an extended timeon-stream (TOS) under O₂-lean conditions. Figure 5 shows X_{n-1} C4H10 and product selectivity of hBN with for 100 hr TOS at 550°C with a *P*_{*n*-C4H10}:*P*_{O2} of 16:1 and *WHSV*⁻¹ of 55.0 kg_{cat} s mol_{*n*-C4H10}⁻¹. No loss of activity was observed in this period; moreover, $X_{n-C4H10}$ even increases slightly with TOS from 11.5% to 13.7%. High selectivity to ethylene (24.2%) and propylene (43.9%) is maintained over the course of the experiment and total COx selectivity remained at 1.2%.

Despite the lack of deactivation in the TOS experiment, coke deposition was still assessed through Raman spectroscopy and TGA. Fresh hBN catalysts were treated for 48 hr at 550°C with a feed of 0.20 atm *n*-butane with either P_{02} of 0.0125 or 0.10 atm. Additionally, contact time was altered to achieve different levels of X₀₂. Raman spectroscopy reveals that catalysts treated under conditions of limited O₂ availability (*i.e.* low P_{O2} and/or high X_{O2}) exhibited two D bands (disordered carbon) at 1180 and 1280 cm⁻ in addition to a G band (graphitic carbon) at 1600 cm⁻¹, respectively (Figure S8).^[42] These bands were less pronounced under O2-richer conditions, suggesting that coke deposition is hindered by high O2 availability. TGA of the catalysts under flowing air was then used to quantitatively determine the amount of coke present after each treatment (Figure S9). After the initial loss in mass on spent catalysts due to dehydration from 100 to 300°C, the loss of mass due to the oxidation of coke deposits at 500 to 700°C shows that no more than 0.25 wt% of the catalysts is comprised of coke deposits. Raman spectroscopy was used to evaluate the catalyst that underwent the largest mass decrease in the oxidative TGA analysis and previously exhibited the largest evidence for coke deposition in the Raman experiment (P_{O2} = 0.0125 atm, X_{02} = 82%). The post-TGA spectrum indicates that these bands significantly decrease in intensity after treatment in flowing air, confirming that these bands can be correctly assigned to coke deposition and that the coke can be oxidatively removed. Although we have no indication that these minor coke deposits affect the catalyst performance at lab scale, they may become an issue with longer TOS at pilot scale.

Conclusions

In this contribution, hBN is established as a selective catalyst for the oxidative cracking of *n*-butane to lighter olefins. The adjustment of reactant feed from O₂-rich to O₂-lean alters the product distribution in the oxidation of alkanes over hBN from primarily butenes (ODH products) to ethylene and propylene (cracking products), respectively. Lowering the O₂ concentration in the feed also reduces the selectivity to CO_x to less than 2% in

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most cases. Increasing reaction temperature allows for enhanced rates of production of cracking products. The rate of product formation as a function of P_{O2} reflects what we hypothesize to be a surface-initiated gas phase radical mechanism, further supported by observations that the previously studied Li₂O/Dy₂O₃/MgO catalyst shares highly similar trends in product formation rates. We propose a reaction mechanism for oxidative cracking over hBN that accounts for our observations in selectivity and rates of formation. There is evidence for slight coke deposition in used samples but there is no observed catalyst deactivation.

As other boron-containing catalysts (B₄C, WB, NiB, etc.) with oxidized surface boron species catalyze the oxidative dehydrogenation (ODH) of alkanes with the same selectivity as hBN,^[25] we envision that these materials will follow the same trends in reactivity observed for hBN when evaluated for their performance in oxidative cracking. Therefore, boron-containing materials are a highly versatile platform for selective hydrocarbon oxidations and new materials can be engineered to meet the needs of new oxidative technology.

Although current hydrocarbon cracking processes are well established, their high emission of CO_2 necessitates the development of environmentally benign technology. Here, we demonstrate that hBN is able to produce light olefins selectively at milder temperatures than steam cracking with an order of magnitude less CO_2 selectivity than previously studied oxidative cracking catalysts. Moreover, the tunability in product distribution with simple adjustment of process parameters enables the flexible production of olefins in a given market. The understanding of the parameters involved in the production of ethylene and propylene from *n*-butane over hBN can inform future studies investigating the oxidation of more complex hydrocarbon feeds as we look toward more efficient routes to valuable chemicals.

Experimental Section

Catalytic Testing

Fresh hBN was obtained from Sigma-Aldrich and not further chemically treated prior to catalytic testing. The powder was pelletized, crushed and sieved to collect particles of 425–600 μ m in diameter in order to limit any potential mass transfer effects. About 300 mg of hBN was loaded into a quartz tube reactor (9 mm ID) undiluted and supported on a bed of quartz wool approximately 1 in. in length in the middle of the tube. A quartz rod was placed beneath the catalyst bed to reduce dead volume and minimize the potential for homogeneous gas-phase reactions past the catalyst bed. Flowrates of *n*-C₄H₁₀ (instrument grade, Matheson), O₂ (UHP, Airgas) and N₂ (UHP, Airgas) were controlled using three mass flow controllers (Bronkhorst) calibrated to each individual gas to allow total flowrates of 40–140 mL min⁻¹ and *WHSV*⁻¹ values ranging from 15.7–55.0 kg_{cat} s mol_{*n*-C4H10}⁻¹. All reactions were performed at a *P*_{tot} of 1 atm. The temperature was controlled using a thermocouple inserted into the middle of the catalyst bed.

Exposure of fresh hBN to reaction conditions results in an induction period of approximately 18 hr before steady state activity is achieved; therefore,

each catalyst was pretreated under identical conditions prior to the collection of reported data. Fresh hBN was heated to 550°C under flow of 20 mL min⁻¹ O₂ and 20 mL min⁻¹ N₂. After the temperature stabilized, the gas flow was changed to a mixture of 2:1:7 n-C₄H₁₀:O₂:N₂ at a flow rate of 80 mL min⁻¹ and the catalyst was treated under this condition for 24 hr. The temperature and gas flow rates were then adjusted to give the desired reaction conditions.

The H₂O produced from the reaction was condensed using a thermoelectrically-cooled condenser held at -5°C. The dried reactor effluent was monitored using an on-line μ GC (Inficon Micro GC Fusion Gas Analyzer) equipped with three GC modules and three micro thermal conductivity detectors. O₂, N₂, CH₄, and CO were analyzed using a Rt-Molsieve 5A column, CO₂ was analyzed using an Rt-U-Bond column, and all hydrocarbons with the exception of CH₄ were analyzed using an Rt-Alumina Bond/Na₂SO₄ column. Reported experiments showed the carbon balance closed within ±5%.

Material Synthesis

The Li₂O/Dy₂O₃/MgO catalyst was synthesized based upon a literature procedure.^[9] To achieve a nominal loading of 7.7 wt% Li₂O and 7.3 wt% Dy₂O₃ on MgO, 1.8 g LiNO₃ (Sigma-Aldrich) , 0.37g Dy₂O₃ (Strem Chemicals), and 4.2 g MgO (Aldrich) were added to 250 mL 18 M Ω H₂O and the resultant slurry was stirred for 2 hr. The mixture was then rotovapped to dryness and dried at 100°C overnight before being ground and treated under flow of air for 2 hr at 200°C. The material was ground again and then heated under for flow of air to 750°C at a rate of 4 C min⁻¹ and held at 750°C for 3 hr. The powder was then prepared and tested as described for hBN, with the pretreatment performed at 575°C.

Thermogravimetric Analysis (TGA)

TGA was performed using a Mettler Toledo DSC/TGA 1 Thermogravemetric Analyzer. About 70-100 mg of used catalysts were deposited into a ceramic 150 μ L crucible. The change in mass was monitored over time as the sample was heated 10°C min⁻¹ from ambient temperature to 900°C under air flow of 40 mL min⁻¹.

Raman Spectroscopy

Raman spectra were recorded by using an Invia Reflex Raman Microscope (Renishaw) equipped with a λ = 785 nm laser. All of the measurements were carried out at ambient conditions using pelletized samples without dilution. Typically, 60 scans of 1 s in duration were averaged. The spectrum was recorded between 600–1700 cm⁻¹ using the WiRE software package (Renishaw).

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Keywords: hexagonal boron nitride • oxidative cracking • oxidation • radicals • hydrocarbon upgrading

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