Supporting Information

Multiple Promotional Effects of Vanadium Oxide on Boron Nitride for Oxidative Dehydrogenation of Propane

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1 Materials used for catalyst preparation

Boric acid, H₃BO₃, (99.999%) and ammonia metavanadate, NH₄VO₃, (99.0%) were purchased from Sigma-Aldrich. The amorphous fumed silica (99.8%) was purchased from the Cabot Corporation. Fumed silica was pretreated in H₂O with vigorous stirring at 90 °C for 3 h, followed by drying at 100 °C overnight. Other chemicals were used as received without purification.
2 Calculations of mass and heat transfer

Mass transfer limitation

The absence of mass transport resistances was checked by a) Weisz-Prater criterion (CWP) for internal diffusion and b) Mears’ criterion (CM) for external diffusion.\(^1\)\(^2\)

a) If \( C_{WP} = \frac{-r'_{A,obs}}{D_e C_{A_S}} < 1 \), then internal mass transfer effects can be neglected.

| Term              | Physical meaning                                  | Unit          | Value          |
|-------------------|--------------------------------------------------|---------------|----------------|
| \(-r'_{A,obs}\)   | Observed reaction rate\([a]\)                     | kmol kg\(_{cat}\)\(^{-1}\) s\(^{-1}\) | \(2.51\times10^{-6}\) |
| \(\rho_c\)        | Solid catalyst density                            | kg m\(^{-3}\) | 2270           |
| \(R\)             | Catalyst particle radius\([b]\)                  | m             | \(1.1\times10^{-5}\) |
| \(C_{A_S}\)       | Gas concentration of A at the catalyst surface, A= propane | kmol m\(^{-3}\) | \(1.1\times10^{-3}\) |
| \(D_e\)           | Effective gas-phase diffusivity                  | m\(^2\) s\(^{-1}\) | \(8.9\times10^{-6}\) |

\([a]\) Taking the highest C\(_3\)H\(_8\) conversion attained on 0.5V/BN-T at 580 °C as the example.
\([b]\) Taking the average mesh size 70 as an example.

Applying corresponding values into the equation gave \( C_{WP} = 7.1\times10^{-5} < 1 \). Therefore, the internal diffusion effect can be neglected.

b) If \( C_{M} = \frac{-r'_{A,obs} \rho_b R n}{k_c C_{A_S}} < 0.15 \), then external mass transfer effects can be neglected.

| Term              | Physical meaning                                  | Unit          | Value          |
|-------------------|--------------------------------------------------|---------------|----------------|
| \(-r'_{A,obs}\)   | Observed reaction rate\([a]\)                     | kmol kg\(_{cat}\)\(^{-1}\) s\(^{-1}\) | \(2.51\times10^{-6}\) |
| \(\rho_b\)        | Bulk density of catalyst bed                     | kg m\(^{-3}\) | 1127           |
| \(R\)             | Catalyst particle radius\([b]\)                  | m             | \(1.1\times10^{-5}\) |
| \(n\)             | Reaction order\([c]\)                            | ---           | 1 or 2         |
| \(C_{A_S}\)       | Gas concentration of A at the catalyst surface, A= propane | kmol m\(^{-3}\) | \(1.1\times10^{-3}\) |
| \(k_c\)           | Mass transfer coefficient                        | m s\(^{-1}\) | \(6.3\times10^{-2}\) |

\([a]\) Taking the highest C\(_3\)H\(_8\) conversion attained on 0.5V/BN-T at 580 °C as the example.
\([b]\) Taking the average mesh size 70 as an example.
As reported, the O₂-ODHP proceeds through ER mechanism and MvK mechanism on BN and VOₓ, respectively. On BN, the reaction order is second-order dependent on the partial pressure of C₃H₈, while is first-order in the case for VOₓ. Therefore, both 1 and 2 were applied in the calculations.

Applying corresponding values into the equation gave \( C_M = 4.5 \times 10^{-4} \) and \( 9.0 \times 10^{-4} \) for second-order and first-order reaction, respectively, both of which are much less than 0.15. Therefore, the external diffusion effect can be neglected.

c) The absence of heat transfer was checked by Mears’ criterion.

\[
\frac{-\Delta H_r (-r'_A) \rho_b R E}{h_t T_b^2 R_g} < 0.15
\]

| Term                  | Physical meaning                        | Unit       | Value         |
|-----------------------|-----------------------------------------|------------|---------------|
| \( -r'_{A, \text{obs}} \) | Observed reaction rate\(^{[a]}\)        | mol kg\text{cat}⁻¹ s⁻¹ | 2.51×10⁻³    |
| \( \rho_b \)         | Bulk density of catalyst bed            | kg m⁻³     | 1127          |
| \( R \)              | Catalyst particle radius\(^{[b]}\)      | m          | 1.1×10⁻⁵      |
| \( E \)              | Activation energy                       | kJ mol⁻¹   | 236.2         |
| \( h_t \)            | Heat transfer coefficient between gas and pellet | kJ m⁻² K⁻¹ s⁻¹ | 0.76          |
| \( T_B \)            | Bulk gas temperature                    | K          | 853           |
| \( R_g \)            | Gas constant                            | kJ mol⁻¹ K⁻¹ | 8.314×10⁻³   |

\(^{[a]}\) Taking the highest C₃H₈ conversion attained on 0.5V/BN-T at 580 °C as the example.
\(^{[b]}\) Taking the average mesh size 70 as an example.

Applying corresponding values into the equation gave \( 1.9 \times 10^{-4} < 0.15 \). Therefore, the heat transfer limitation can be neglected.
3 Additional activity results for O₂-ODHP reaction

**Blank test for O₂-ODHP.** For comparison, the blank test was performed on respective quartz sand (diluent) and quartz wool in C₃H₈/O₂/He (1/1/38) at 600 °C with GHSV = 18000 mL g⁻¹ h⁻¹. C₃H₈ conversion is 2.8 and 3.6%, respectively, the contribution of which is limited if compared with the conversion obtained on BN-T (i.e., 38.2%) and 0.5V/BN-T (i.e., 68.7%) under the same reaction conditions. The same blank test was also conducted on SiO₂ under identical conditions. The C₃H₈ conversion is ca. 2.1% at 600 °C, the contribution is limited in comparison to that of BOₓ/SiO₂ catalysts.
Figure S1. Light alkene (C$_2$-C$_3$) selectivity-C$_3$H$_8$ conversion relationship (A) and temperature-dependent changes in C$_3$H$_6$ yield (B) on VO$_x$/BN-T catalysts for O$_2$-ODHP reaction. Reaction conditions for O$_2$-ODHP: C$_3$H$_8$/O$_2$/He (1/1/38), GHSV= 18000 mL g$^{-1}$ h$^{-1}$.
Figure S2. Temperature-dependent changes in C$_3$H$_8$ conversion (A), light-alkene selectivity (C$_2$-C$_3$) (B) and yield (C) of 0.5V/BN-T from three consecutive light-off tests. Reaction conditions for O$_2$-ODHP: C$_3$H$_8$/O$_2$/He (1/1/38), GHSV = 18000 mL g$^{-1}$ h$^{-1}$. 
Figure S3. Temperature-dependent changes in C\textsubscript{3}H\textsubscript{8} conversion (A), light-alkene (C\textsubscript{2}-C\textsubscript{3}\textsuperscript{−}) yield (B), and plotted light-alkene selectivity-C\textsubscript{3}H\textsubscript{8} conversion relationship (C-D) on 0.5V/SiO\textsubscript{2}, BN-T, the physical mixture of 0.5V/SiO\textsubscript{2} and BN-T (weight ratio, 1/1), and 0.5V/BN-T for O\textsubscript{2}-ODHP reaction. Reaction conditions for O\textsubscript{2}-ODHP (A-C): C\textsubscript{3}H\textsubscript{8}/O\textsubscript{2}/He (1/1/38), GHSV= 18000 mL g\textsuperscript{−1} h\textsuperscript{−1}. 
Figure S4. Temperature-dependent changes in C\textsubscript{3}H\textsubscript{8} conversion (A), light-alkene (C\textsubscript{2}-C\textsubscript{3=}) yield (B), and plotted light-alkene selectivity-C\textsubscript{3}H\textsubscript{8} conversion relationship (C-D) on 1V/SiO\textsubscript{2}, 5BO\textsubscript{5}/SiO\textsubscript{2}, the physical mixture of 1V/SiO\textsubscript{2} and 5B/SiO\textsubscript{2} (weight ratio, 1/1), and 1V/5B/SiO\textsubscript{2} for O\textsubscript{2}-ODHP reaction. Reaction conditions for O\textsubscript{2}-ODHP (A-C): C\textsubscript{3}H\textsubscript{8}/O\textsubscript{2}/He (1/1/38), GHSV=18000 mL g\textsuperscript{-1} h\textsuperscript{-1}.
Figure S5. Effect of C₃H₈ composition % on C₃H₈ conversion rate on BN-T at 540 °C. Reaction conditions: 0.4-2.5% C₃H₈/2.5% O₂, balanced in He and Ar, GHSV= 24000 mL g⁻¹ h⁻¹.

Reaction order of C₃H₈: 1.8

R²= 0.9999
Figure S6. Effect of O₂ composition % on C₃H₈ conversion rate of 0.5V/BN-T at 540 °C. Reaction conditions: 0.4-2.5% O₂/2.5% C₃H₈, balanced in He and Ar, GHSV= 24000 mL g⁻¹ h⁻¹.
4 Additional characterization results

Figure S7. SEM images of BN, BN-T, and VOₓ/BN-T catalysts.
Figure S8. XRD patterns of VOₓ/BN-T catalysts and that of the benchmark BN-T.

The pattern of h-BN (BN-T in the figure) displays all expected peaks, implying its high crystallinity. The peaks at 2θ of 26.9, 41.8, 44.0, 50.3, and 55.2° correspond to crystallographic (002), (100), (101), (102), and (004) families of planes in h-BN, respectively (JCPDS file 034-0421). The diffraction peaks of VOₓ are absent in both 0.5V/BN-T and 1.0V/BN-T due to the nanocrystalline/amorphous nature and lower loadings of vanadium. Diffraction peaks of crystalline V₂O₅ (JCPDS 9-387) are absent either.
Figure S9. Raman spectra of fresh BN and BN-T pretreated in C₃H₈/O₂ atmosphere (1/1) at 600 °C for 12 h in the region of 600-1100 cm⁻¹. All spectra were collected in air at room temperature.
Figure S10. Raman spectra of fresh and spent BN and 0.75V/BN-T in the region of 1340-1400 cm\(^{-1}\). All spectra were collected in air at room temperature. Spent catalysts were collected after ODHP reaction from 480-600 °C.
Raman spectra of 5B/SiO₂ (A), and 1V/5B/SiO₂ (B-C) under various conditions, along with the spectrum of support SiO₂ as a reference for each figure. The spectra denoted as “C₃H₈/O₂-550 °C” represent the spectra collected by in situ Raman measurements with similar conditions as activity tests, namely C₃H₈/O₂=1, 30 mL min⁻¹, 30 min; the ones denoted as “Spent O₂-RT” were acquired based on the spent catalysts collected after the activity tests with the temperature range of 520-560 °C by using AMI 200. For clarity, the spectra of fresh and spent 1V/5B/SiO₂ were amplified in (C).
The Raman spectrum of the spent 0.75V/BN-T, collected after O2-ODHP reaction, shows a new band at 882 cm\(^{-1}\), which can be attributed to the borate species with hydroxylated nonring boron (B-OH) (Figure 3B).\(^3\) For comparison, BO\(_x\)/SiO\(_2\) and VO\(_x\)/BO\(_x\)/SiO\(_2\) were prepared, and a similar band is observed on both fresh and spent catalysts, as shown in Figure S11. These species are susceptible to reaction conditions and may disappear for both BN and BO\(_x\) catalysts, which is in line with the literature.\(^3\) Our recent DFT calculations suggest that the surface O-H groups on BO\(_x\) play a critical role in the initial C-H bond activation, in which O\(_2\) is reduced to HO\(_2\) by abstracting the hydrogen from surface O-H, resulting in the formation of weakly-bonded B-HO\(_2\) and B-C\(_3\)H\(_7\) on adjacent BO\(_x\) sites.\(^4\) A recent work has evidenced the existence of B-OH borate in proximity to Si-OH species on BO\(_x\)/SiO\(_2\), which are putative active sites for ODHP reaction.\(^3\) The Raman results in this work are consistent with these previous works, again demonstrating the pivotal role of BO\(_x\), formed through surface oxyfunctionalization, in catalyzing propane dehydrogenation in O\(_2\).


5 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) at the vanadium K edge (5465 eV) was measured at the materials research collaborative access team bending magnet line (10-BM) of the advanced photon source, Argonne National Laboratory. Catalysts were measured in transmission mode using a set of three ion chambers, which allowed for simultaneous measurement of a sample and a V foil energy reference. Samples were ground into a fine powder and pressed into a self-supporting wafer inside of a stainless steel sample holder. Samples were treated in a quartz-tube reactor with Ultra-Torr end caps fitted with valves for gas flow and x-ray transparent windows. Catalysts were pretreated at 500 °C in 3% O₂/He and 3% C₃H₈/He and mixtures thereof for 30 min before being cooled to room temperature under gas flow. The atmosphere was then sealed in the reactor for measurement. Table S1 lists the samples and treatments for V-BN catalysts and reference compounds purchased from Sigma-Aldrich.

Table S1. Vanadium catalysts with treatment details and vanadium reference compounds.

| Sample       | Note                                      |
|--------------|-------------------------------------------|
| Fresh 1.0V/BN-T | In situ XAS, 500°C, 3% O₂/He → 3% C₃H₈ → 3% O₂/He |
| Fresh 1.0V/BN-T | In situ XAS, 500°C, 3% C₃H₈/He & 3% O₂/He         |
| V metal      | BCC V⁰                                      |
| V(AcAc)₃     | D₃ V³⁺                                      |
| V₂O₃         | Distorted O₈ V³⁺                             |
| VB₂          | V⁴⁺ with 12 B nearest neighbors              |
| VO₂          | Distorted O₈ V⁴⁺                             |
| V₂O₅         | C₄v V⁵⁺                                     |
| NH₄VO₃       | Distorted T₄ V⁵⁺                             |

Data reduction was performed using the Athena program from the Demeter software suite. R space EXAFS spectra were produced taking the Fourier transform of k² weighed data over a k range of 3-8 Å⁻¹. XANES pre-edge analysis was performed using the XAS viewer GUI contained in the python package xraylarch. The pre-edge peak was fit using constant width gaussians and the rising edge background was fit using a Lorentzian peak and a first order polynomial.
Pre-edge peak areas were normalized based on the pre-edge peak area for NH₄VO₃, which is a V⁵⁺ compound with a distorted tetrahedral structure. The centroid of the background subtracted pre-edge peak was calculated as the first moment of the distribution. Pre-edge peak centroids were normalized to the threshold energy for vanadium metal (5465 eV). Reported errors in normalized pre-edge peak area and pre-edge centroid are calculated from peak fits performed in xraylarch.

Results and discussion

Figure S12 shows the normalized V K edge XANES for vanadium reference compounds. In general, the pre-edge, shakedown transition energy, and main edge increase in energy with oxidation state. The energy and shape of the above mentioned features also change with the coordination in compounds of the same oxidation state, which can be seen in the spectra of V₂O₃ and V(ACAc)₃ or V₂O₅ and NH₄VO₃.

![Figure S12](image1)

**Figure S12.** Vanadium K edge (A) and pre-edge (B) XANES for vanadium reference compounds.

Figure S13 shows the V K edge XANES for 1.0V/BN-T after consecutive treatments in O₂, C₃H₈, C₃H₈/O₂, and O₂ regeneration at 500 °C. Two *in situ* experiments were performed on this catalyst. In the first measurement, the fresh sample was sequentially treated at 500°C in O₂ →
C\textsubscript{3}H\textsubscript{8} \rightarrow O\textsubscript{2}, and the resultant spectra are noted as O\textsubscript{2}, C\textsubscript{3}H\textsubscript{8}, and O\textsubscript{2}-regenerated in the figure, respectively. This was done to determine if vanadium can undergo reversible redox under the reaction conditions for direct dehydrogenation of propane (DHP). In the second \textit{in situ} measurement, the same sample was measured under a mixture of C\textsubscript{3}H\textsubscript{8}/O\textsubscript{2} (1/1) at 500 °C to determine the predominant oxidation state of vanadium under steady-state reaction conditions of O\textsubscript{2}-ODHP. This sample is noted in figures as C\textsubscript{3}H\textsubscript{8}/O\textsubscript{2}.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{FigureS13.png}
\caption{V K edge XANES for fresh 1.0V/BN-T after consecutive treatments in O\textsubscript{2}, C\textsubscript{3}H\textsubscript{8}, and O\textsubscript{2} regeneration at 500 °C (A) and that for a single treatment in C\textsubscript{3}H\textsubscript{8}/O\textsubscript{2} (B). Spectra of reference compounds are also plotted for comparison.}
\end{figure}

The catalyst in O\textsubscript{2} alone and the one in C\textsubscript{3}H\textsubscript{8}/O\textsubscript{2} have XANES spectra that almost completely overlap (Figure S13). This suggests that under reaction conditions the oxidation state of V is like that in the case of the O\textsubscript{2}-treated catalyst in the initial 30-min time-on-stream (TOS). The catalyst treated in C\textsubscript{3}H\textsubscript{8} alone shows a strong decrease in the intensity of the pre-edge peak and a shift to lower energy. This demonstrates a decrease in the oxidation state of vanadium in the catalyst. A subsequent treatment of C\textsubscript{3}H\textsubscript{8}-treated catalyst in O\textsubscript{2} returns the vanadium to the more
oxidized state, largely matching that of the initially $O_2$-treated catalyst. Clearly, the redox cycles present under the ODHP reaction.
| Sample                      | Threshold energy (eV) | Pre-edge peak centroid (eV) | Normalized pre-edge peak area | Edge energy (eV) | White line energy (eV) |
|-----------------------------|-----------------------|-----------------------------|------------------------------|-----------------|------------------------|
| VB₂                         | 5466.8                | 5469.2±0.02                 | 0.25±0.02                    | 5474.6          | 5484.5                 |
| V₂O₃                        | 5467.6                | 5469.2±0.02                 | 0.333±0.007                  | 5475.5          | 5488                   |
| VO₂                         | 5468.4                | 5470.2±0.02                 | 0.346±0.005                  | 5479.2          | 5491.5                 |
| V₂O₅                        | 5469.6                | 5470.9±0.007                | 0.71±0.01                    | 5481.2          | 5494.4                 |
| V(AcAc)₃                    | 5467.3                | 5468.5±0.03                 | 0.0695±0.0003                | 5477.9          | 5484.1                 |
| NH₄VO₃                      | 5468.8                | 5469.8±0.04                 | 1±0.1                        | 5482.4          | 5494.3                 |
| 1.0V/BN-T in O₂[a]          | 5469.5                | 5470.4±0.007                | 0.84±0.02                    | 5481.1          | 5494.7                 |
| 1.0V/BN-T in C₃H₈[a]        | 5468.6                | 5469.9±0.007                | 0.57±0.03                    | 5479.6          | 5491.4                 |
| 1.0V/BN-T in C₃H₈/O₂[a]     | 5469.6                | 5470.4±0.006                | 0.86±0.01                    | 5481.1          | 5497.4                 |
| 1.0V/BN-T in O₂, regenerated[a] | 5469.4            | 5470.3±0.005                | 0.87±0.02                    | 5481.1          | 5494.3                 |

[a] Based on the *in situ* XAS experiments on fresh 1.0V/BN-T catalysts.
Figure S14. R-space EXAFS spectra of V-BN catalysts after treatments in O₂ and C₃H₈ plotted with reference compounds.
6 Synchrotron vacuum ultraviolet photoionization mass spectroscopy

Synchrotron vacuum ultraviolet photoionization mass spectroscopy (SVUV-PIMS) measurements were carried out at the combustion end station of beamline 03U in the National Synchrotron Radiation Laboratory (Hefei, China). A quartz catalytic reactor was connected to the SVUV-PIMS spectrometer, where the catalyst bed (2×2 mm) was placed 20–30 mm from the sampling nozzle of the spectrometer. All the samples were pretreated by ODHP reaction feed gas (C$_3$H$_8$:O$_2$:He = 1:1:38, total flow rate 30 mL min$^{-1}$) with atmospheric pressure at 500 °C for 12 h before the SVUV-PIMS measurements. During the ODHP reaction, the reaction gas, consisting of C$_3$H$_8$ (flow rate: 15 sccm), O$_2$ (flow rate: 15 sccm), and Ar (flow rate: 70 sccm), (C$_3$H$_8$ : O$_2$ = 1:1), was fed to a mixing chamber, and then the gas mixture was pumped through the catalyst bed at a total pressure of 2 Torr. After the catalytic reaction reached steady state at the desired temperature, the composition of the effluent gas was analyzed by the online SVUV-PIMS spectrometer. A homemade time-of-flight mass spectrometer (TOF-MS) with a mass resolution of 3000 was used, and the m/z value was calibrated based on the flight time of hydrogen (m/z= 2.016), water (m/z= 18.011), carbon monoxide (m/z= 27.995), oxygen (m/z= 31.990), and carbon dioxide (m/z= 43.990). Identification of these species under various photon energies was discussed explicitly in our recent work.$^2$
Figure S15. SVUV-PIMS spectra of the gas-phase components for the blank test at 600 °C (A) and for ODHP reaction on 1.0V/BN-T catalysts at room temperature (B). Photon energy= 10 eV.

For comparison, a blank test was conducted at 600 °C, and no products are observed in the gas phase, except the fraction of propane (Figure S15A). Also, a reference spectrum was acquired at room temperature on 1.0V/BN-T prior to temperature elevation. The resultant spectrum confirms that no products exist in the gas phase (Figure S15B). These observations imply that the presence of BN-based catalysts contribute to the all detected species in gas phase on both BN-T and 1.0V/BN-T under reaction conditions derive from the catalyst.
7 Additional activity results for NO-assisted O$_2$-ODHP reaction

**Blank test for NO-assisted O$_2$-ODHP.** The activity test of NO-assisted O$_2$-ODHP was performed on quartz wool-filled bed at the temperature range of 480-600 °C. 5% C$_3$H$_8$/He and 5% O$_2$/He were used with a C$_3$H$_8$/O$_2$ ratio of 1. Additional NO was introduced by using 0.1% NO/He, and the concentration was 350 ppm. The overall GHSV was fixed at 24000 mL g$^{-1}$ h$^{-1}$. The activity performance was shown in **Figure S16**. Although the NO-induced enhancement in activity is significant, VO$_x$/BN-T catalysts still show higher activity under the same reaction conditions, except at 600 °C where the gas-phase reaction dominates.

**Figure S16.** Changes in C$_3$H$_8$ conversion (A) and light-alkenes selectivity (B) of NO-assisted O$_2$-ODHP reaction over quartz wool (blank test) and 0.5V/BN-T. Reaction conditions: C$_3$H$_8$/O$_2$=1, NO=350 ppm, GHSV= 24000 mL g$^{-1}$ h$^{-1}$. 
Figure S17. Temperature-dependent changes in C$_3$H$_8$ conversion (A), light-alkene (C$_2$-C$_3$) yield (B), and selectivity (C) on 0.5V/BN-T for NO-assisted O$_2$-ODHP reaction with additional NO concentrations varying from 180-3500 ppm. Reaction conditions for O$_2$-ODHP: C$_3$H$_8$/O$_2$=1, GHSV=18000 for O$_2$ (w/o additional NO) and 24000 mL g$^{-1}$ h$^{-1}$ (w additional NO in ppm).
**Figure S18.** Light-alkene selectivity-C$_3$H$_8$ conversion relationship of 1V/5B/SiO$_2$ for NO-assisted O$_2$-ODHP reaction. Reaction conditions: C$_3$H$_8$/O$_2$=1/1, additional NO concentrations 350-3500 ppm, GHSV=18000 for O$_2$ (w/o additional NO) and 24000 mL g$^{-1}$ h$^{-1}$ (w additional NO in ppm).
8 X-ray photoelectron spectroscopy

Figure S19. XP spectra of fresh and spent BN-T and 0.75V/BN-T catalysts in the regions of O 1s (A) and V 2p (B).

Table S3. Surface composition by XPS analysis for fresh and spent BN-T and 0.75V/BN-T.

| Catalyst            | Surface composition / at.% |
|---------------------|----------------------------|
|                     | B  | N  | O  | V  | C  |
| Fresh BN-T          | 49.7| 35.5| 4.2| ---| 10.7|
| Spent BN-T<sup>[a]</sup> | 40.4| 27.6| 6.5| ---| 25.5|
| Fresh 0.75V/BN-T    | 41.7| 29.0| 5.6| 0.1| 23.7|
| Spent 0.75V/BN-T<sup>[a]</sup> | 47.3| 32.5| 11.0| 0.1| 9.1|

<sup>[a]</sup> Spent catalysts were collected after 12-h ODHP activity test at 600 °C.
Table S4. Surface composition of N-containing species by XPS analysis for fresh and spent BN-T and 0.75V/BN-T.

| Catalyst                  | Surface composition / at.% |
|---------------------------|----------------------------|
|                           | B-N | N-H |
| Fresh BN-T                | 32.9| 1.0 |
| Spent BN-T\textsuperscript{[a]} | 25.1| 1.4 |
| Fresh 0.75V/BN-T          | 27.2| 0.7 |
| Spent 0.75V/BN-T\textsuperscript{[a]} | 25.8| 5.3 |

\textsuperscript{[a]} Spent catalysts were collected after 12-h ODHP activity test at 600 \textdegree C.
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