Supporting Information

New Insights into the Oxidative Dehydrogenation of Propane on Borate-Modified Nanodiamond

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1. Materials

The ND used in this study (high purity grade) was supplied by Beijing Grish Hitech Co.China, it was purified from the black powder produced by explosive detonation using a nitric acid-sulfuric acid-fuming sulfuric acid mixture. The diamond powder thus obtained has a light brown color with particle sizes of ca. 3-10 nm, and with a phase purity of powder > 98%. In order to remove the unstable disordered carbon on the surface, ND was then thermally annealed in a furnace at 1000 ^{o}C for 4 h under helium flow (defined as AND). The modified catalysts were prepared by incipient-wetness impregnation method. AND was soaked in a controlled amount of $(NH_4)_2B_{10}O_{16}\cdot 8H_2O$ aqueous solution and stirred ultrasonic untill to a near-dryness state. The impregnated samples were then dried in air at 120 ^{o}C overnight.

2. Characterizations

High-resolution transmission electron microscopy (HRTEM) was performed using a FEI Cs-corrected Titan 80-300 microscope and a FEI Tecnai G2 F20 microscope. Thermogravimetric (TG) was performed on NETZSCH STA 449 F3 under a flow of argon or air (50 ml min^{-1}) with a heating rate of 10 °C min^{-1}. Brunauer-Emmett-Teller (BET) and microporous surface area analysis were determined by N_2 physisorption at –196 °C on a Micrometrics ASAP 2020 instrument. The samples were outgassed at 150 ^{o}C for 12 h prior to the isotherm measurement. IR studies were conducted with a Thermo Nicolet iZ10 FTIR system using a diffuse reflectance infrared Fourier-transform (DRIFT) cell that has been extensively modified to allow in-situ

treatments up to 800 °C under flowing gases. The spectra were recorded in the 650–4000 cm^{-1} wavenumber range with 128 scans at a resolution of 4 cm^{-1}. The X-ray photoelectron spectroscopy (XPS) measurements were performed on ESCALAB 250 instrument with Al Kα X-rays (1489.6 eV).

3. Catalytic tests

Oxidative dehydrogenation of propane (ODH) was carried out in a quartz fixed-bed reactor under atmospheric pressure. The reaction products were analyzed by Agilent 7890A gas chromatograph equipped with a flame ionization detector (FID) for hydrocarbon and a thermal conductivity detector (TCD) for inorganic components. Blank experiments showed that reaction rates were negligible without carbon catalyst. In all tests, carbon mass balances were within 100±0.5%.

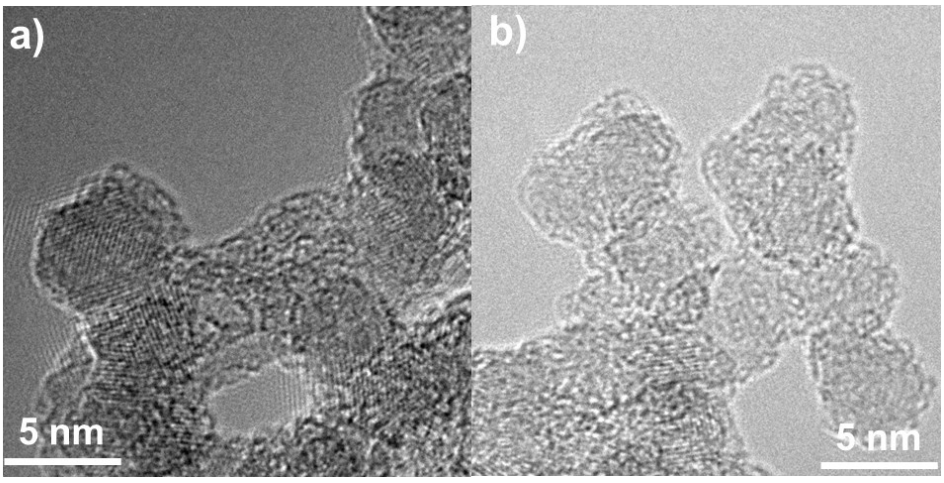

Figure S1 High-resolution TEM images of a) 5B-AND and b) 15B-AND.

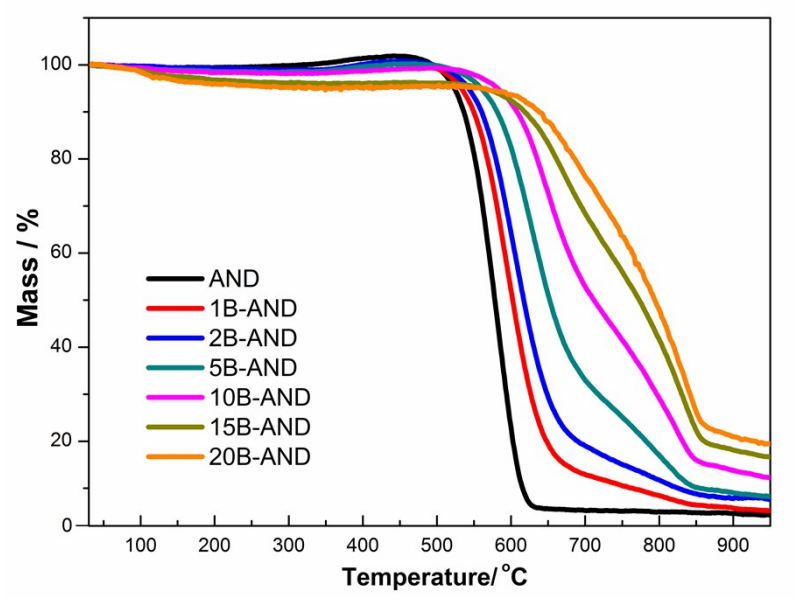

Figure S2 Dynamic TPO curves from room temperature to 950 °C under air flow, 10 °C/min.

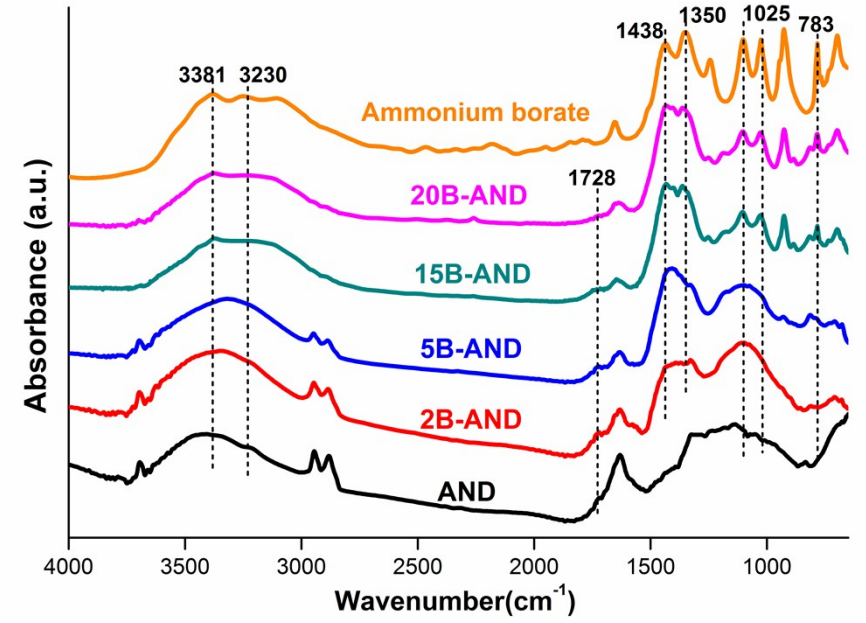

Figure S3 DRIFT spectra of unmodified and borate-modified ANDs, in which the spectrum of ammonium borate was given as reference.

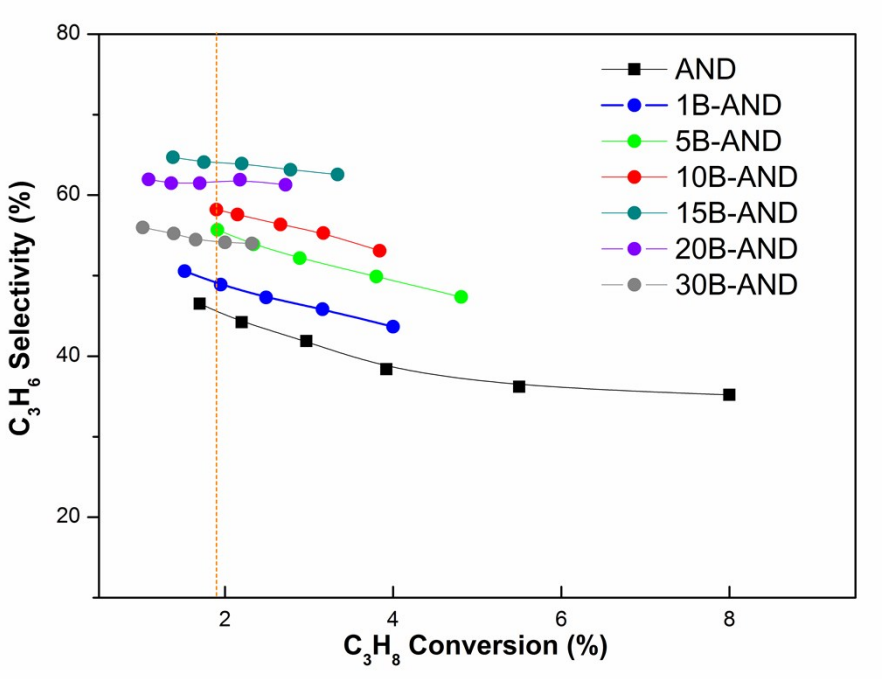

Figure S4 The propene selectivity versus propane conversion obtained by variation of space velocities. Reaction conditions: 450 °C, catalyst weight: 150-180 mg, 3%C_3H_8, 3%O_2, He balance, total flow rate 10-70 ml/min.

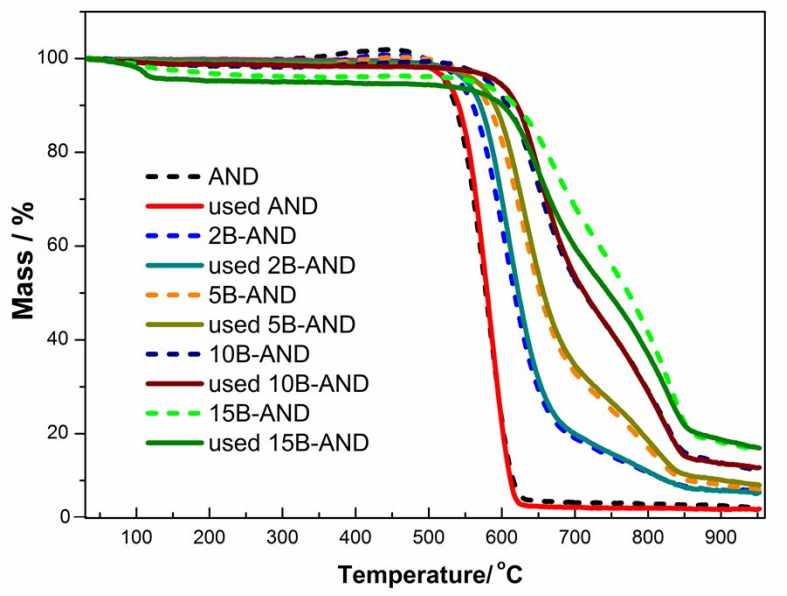

Figure S5 Comparison of dynamic TPO curves of selected samples before and after ODH reaction from room temperature to 950 °C under air flow, 10 °C/min.

Table S1 Porous texture of ANDs after ODH reaction.

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore width (nm)
AND	324	1.43	17.7
2B-AND	323	1.26	15.6
5B-AND	324	1.30	16.0
10B-AND	320	1.17	14.7
15B-AND	295	1.10	15.5
20B-AND	211	0.95	14.2

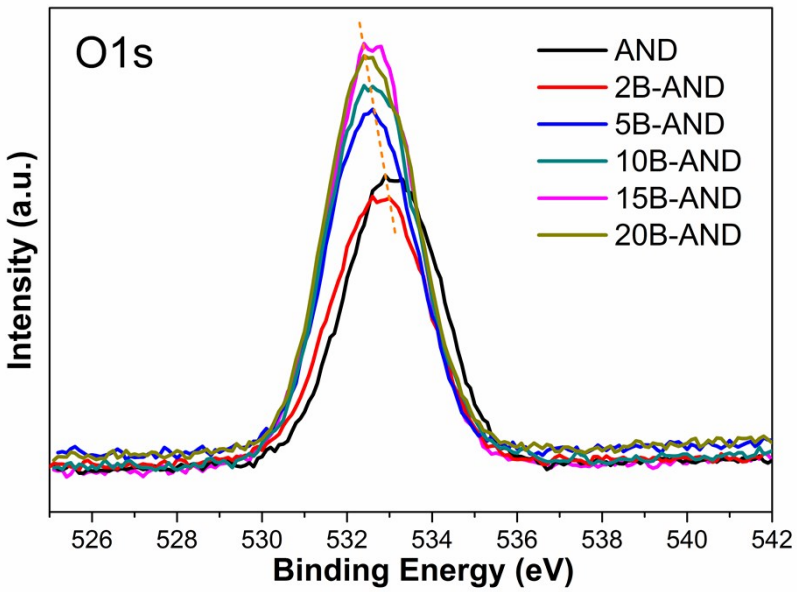

Figure S6 O1s core level spectra of the selected ANDs after catalysis.