Nitrogen Doped Nanocarbon as Metal-Free Catalyst for CO_2 Hydroboration

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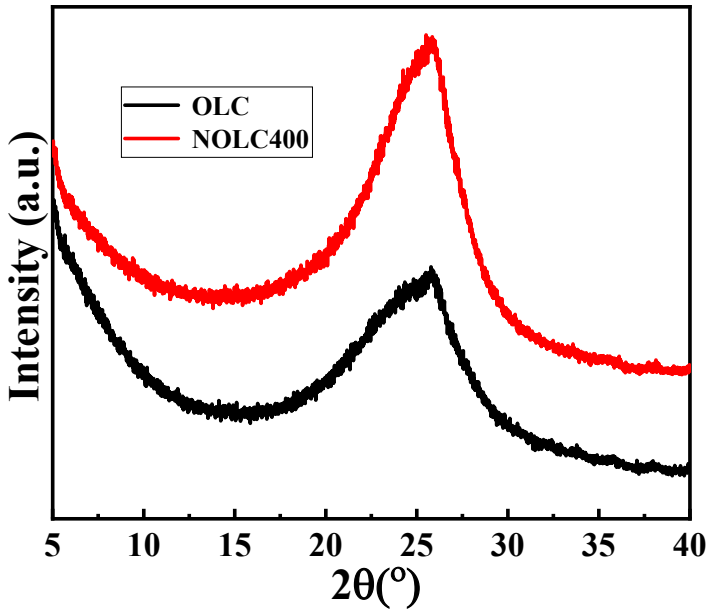

Fig. S1 The XRD spectra of OLC1500 and NOLC400. Collected in X-ray diffractometer (SmartLab 3KW, Rigaku Corporation)

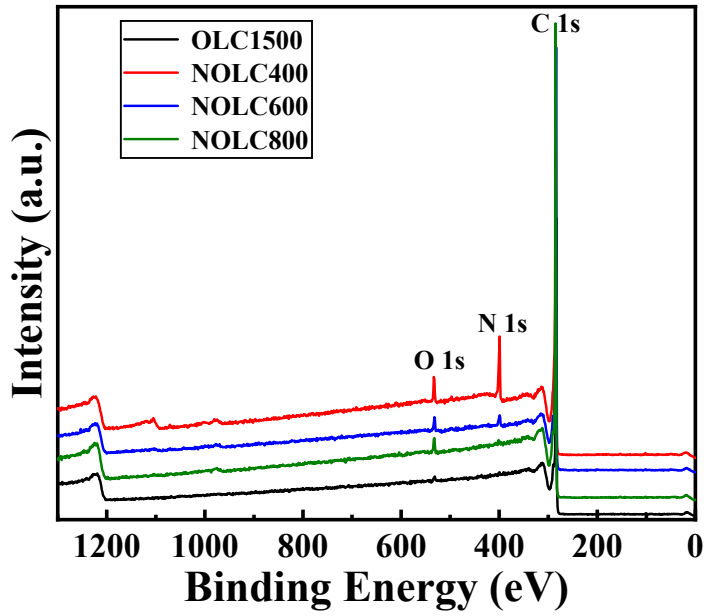

Fig. S2 The XPS survey of OLC1500 and NOLC*x* catalysts

Table S1 Elemental composition of samples from XPS analysis

Sample	C/%	O/%	N/%
OLC	98.3	1.7	-
NOLC400	86.3	3.0	10.7
NOLC600	95.2	2.2	2.6
NOLC800	96.5	2.5	0.9

Table S2 The surface area and porosity of samples

Sample	Surface area m^2/g	Pore Volume cm^3/g	Mean Pore Size nm
OLC	435.7	1.48	13.6
NOLC400	230.7	0.91	15.4
NOLC600	307.8	1.01	14.9
NOLC800	369.1	1.18	12.8

The gas product composition analyzed by GC

The gaseous products from the CO_2 hydroboration catalyzed by NOLC400 are analyzed using the gas chromatography (GC9720 plus, Fuli) equipped with two FID detectors and one TCD detector (reaction condition: 10 mg NOLC400, 2 mmol HBpin, 100 ^oC, 4 MPa CO_2, 2 h). The high-concentration gas products are analyzed using the TCD detector. Low-concentration CO would be transformed into CH_4 and then analyzed using the FID **1** detector. The gaseous hydrocarbons are analyzed by FID **2** detector, such as CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6 and so on. According to the TCD signal, a small amount of H_2 is produced (3200ppm) from the decomposition of borane apart from the reactant CO_2. The small amount of O_2 (1600ppm) and N_2 (11333ppm) are from the leakage of air during sampling. From the FID **1** signal, only negligible amounts of CO and CH_4 are found to be produced during CO_2 hydroboration. Meanwhile, no other gaseous hydrocarbons were generated.

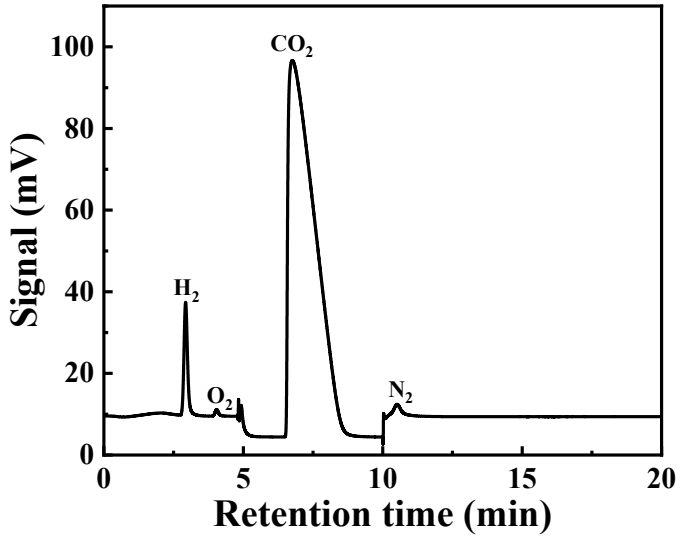

Fig. S3 TCD signal of the gas product

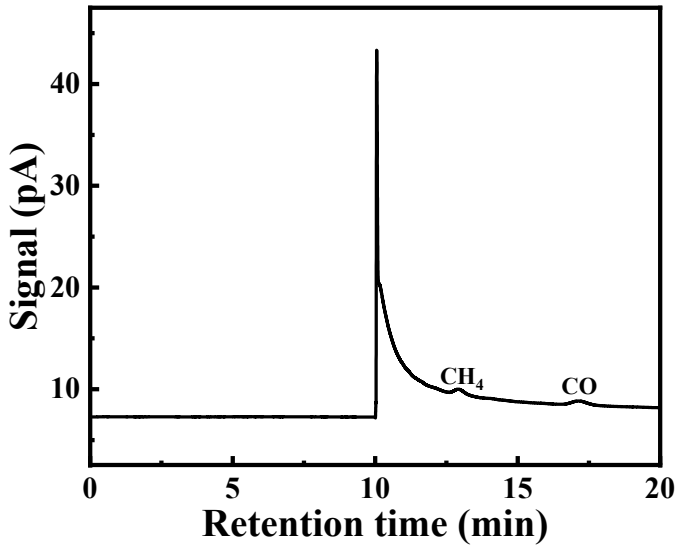

Fig. S4 FID **1** signal of the gas product

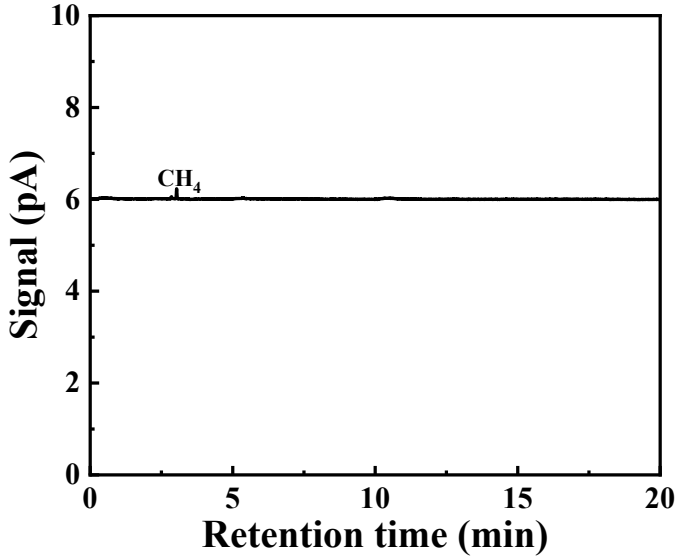

Fig. S5 FID **2** signal of the gas product

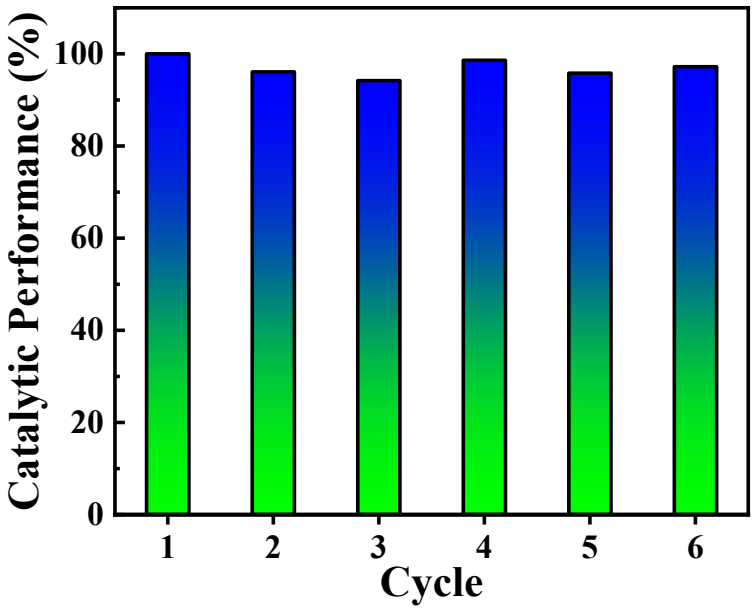

Fig. S6 The recycling performance of NOLC400 catalyst (the catalytic performance in the recycling experiments is normalized by that of fresh NOLC400 catalyst). Reaction condition: 10 mg catalyst, 2 mmol HBpin, 100 °C, 4 MPa CO_2, 2 h. After each reaction, the catalyst was separated from the reaction medium through centrifugation and washed with toluene for the next cycle.

Table S3 The comparation of catalytic performance with the reported catalysts

Entry	Catalyst	TOF/h^{-1}	Catalytic System	Reference
1	$Co(acac)_3$-$NaHBEt_3$	15	Homogeneous	1
2	$PhSi(CH_2PPh)_3$-Co	2.8	Homogeneous	2
3	$NaBH_4$	14.5	Homogeneous	3
4	(^{tBu}PCP)PdH	2.1	Homogeneous	4
5	1-Bcat-2-PPh_2-C_6H_4	17	Homogeneous	5
6	TBD, DBU	0.9, 3.2	Homogeneous	6
7	NOLC400	9.5	Heterogeneous	**This work**

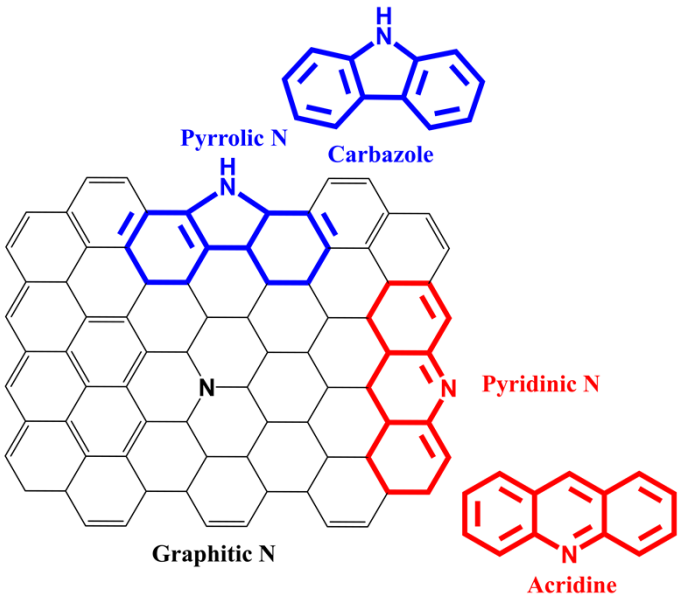

Fig. S7 The structural model of N-doped carbon surface and the aromatic molecules containing specific N species for mimicking the N-doping structure on carbon surface

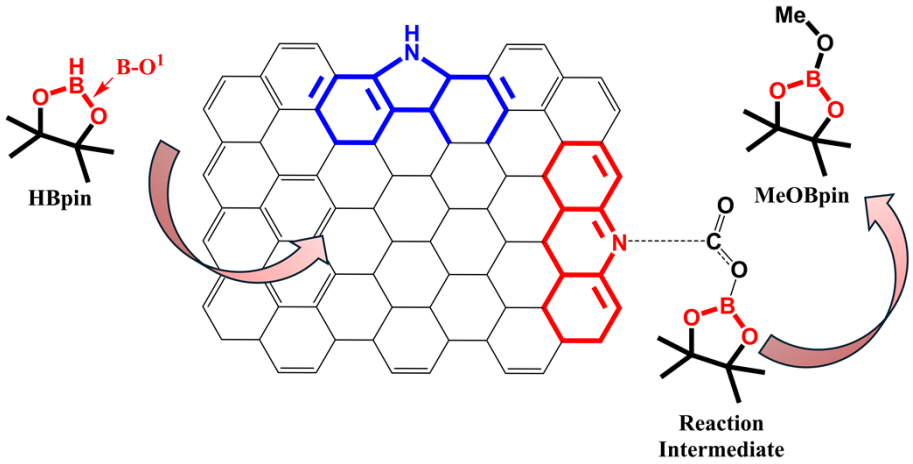

Fig. S8 The indication of B-O[1] structure in the dioxaborolane ring of HBpin whose vibration mode would change in the reaction intermediate and the final product

Reference

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