Supplementary Information:

Dehydration of n-Butanol on Phosphate-Modified Carbon Nanotubes: Active Site and Intrinsic Catalytic Activity

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Catalyst characterizations

The temperature-programmed desorption (TPD) measurement was carried out in He with Pfeiffer Omnistar mass spectrometer for online off-gas (CO: 28, CO_2: 44) analysis. In a typical run, 75 mg catalyst was loaded in a fixed-bed quartz reactor with the inner diameter of 9 mm. Prior to temperature ramping, the weakly adsorbed water was removed in He (10 mL/min) flow at 120 °C for 2 h, and after that the reactor was heated at a rate of 5 °C/min to 900 °C. The ammonia temperature-programmed desorption (NH_3-TPD) measurement was carried out in He with Pfeiffer Omnistar mass

spectrometer for online off gas (NH_3:16) analysis. In a typical run, 75 mg catalyst was loaded in a fixed-bed quartz reactor with the inner diameter of 9 mm. Prior to temperature ramping, the weakly adsorbed water was removed in He (40 mL/min) flow at 100 °C for 1 h, and then the catalyst was cooled down to 30 °C. 10% vol. NH_3 with He balance (40 mL/min) was fed for 1 h. After adsorbing NH_3, pure He was fed (40 mL/min), and the sample was heated at 5 °C/min to 100 °C for 2 h to remove the physically adsorbed ammonia and then cooling down to the room temperature. At last, the system was heated at 5 °C/min to 600 °C, and the desorption product was monitored with the mass spectrometer. The TPD signals were fitted and deconvoluted using the PEAKFIT4.12 software.

The P 2p and O 1s X-ray Photoelectron Spectroscopy (XPS) spectra were measured by an ESCALAB 250 (Thermo VG, USA) set up with Al Ka X-rays (1486.6 eV, 150 W, 50.0 eV pass energy). The P 2p and O 1s XPS spectra were fitted and deconvoluted using Gaussian-Lorentzian function after subtraction of a Shirley background using XPSPEAK41 software. The TEM measurements were performed on an aberration-corrected JEOL ARM 200CF microscope, and SAED and EDX (energy-dispersive x-ray) elemental mapping measurements were performed on the same TEM.

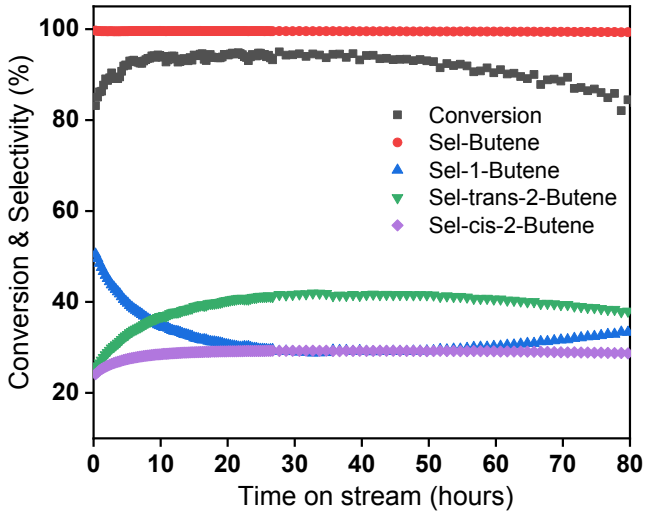

Fig. S1. Long-term catalytic performance of P-oCNT (5% weight) in nB conversion reactions (reaction conditions: 260 °C, 1.0 kPa nB, 18 mL/min total flow rate, He balance, 100 mg catalyst).

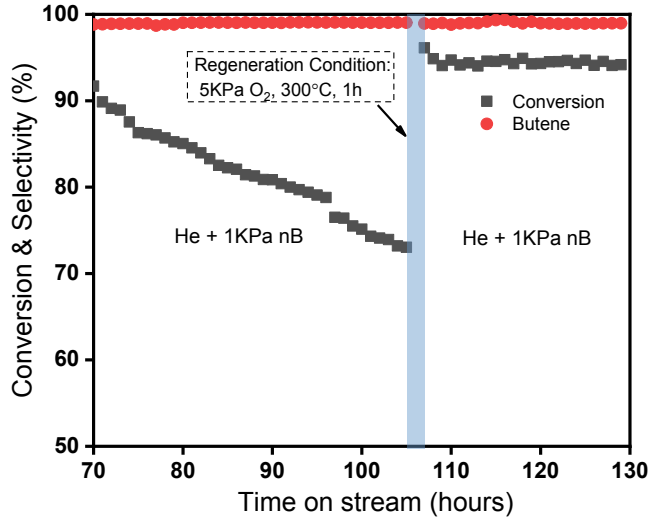

Fig. S2. Catalytic performance of P-oCNT (5% weight) during the regeneration process in nB conversion reactions (reaction conditions: 260 °C, 1.0 kPa nB, 18 mL/min total flow rate, He balance, 100 mg catalyst).

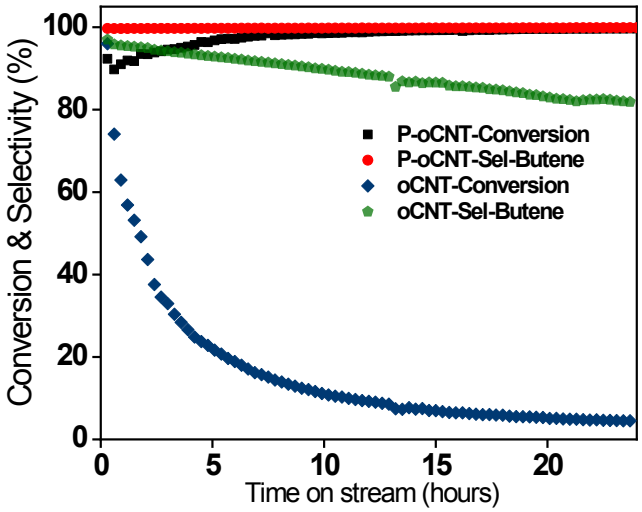

Fig. S3. Catalytic performance of P-oCNT (10% weight) and oCNT in nB dehydration reactions. nB conversion and butene selectivity as a function of reaction time (reaction condition: 260 °C, 1.0 kPa nB, 18 mL/min total flow rate, He balance, 100 mg catalyst).

Table S1. The catalytic activity and reaction condition of the P-oCNT and other catalysts in butanol dehydration reaction.

Catalysts	Weight (g)	Temperature (°C)	Conversion (%)	Butene Selectivity (%)	nB (KPa)	Pressure(bar)	Space Velocities (h^{-1})	TOS (h)	Reference
S/ZrO_2	0.5	200	59.8	94.5	-	1	0.031	0.5	1
AM-11	0.05	250	100	100	-	1	2	20	2
nano-HZSM5	0.2	240	54	78	29	5	-	50	3
γ-Al_2O_3	0.01	240	62	23	29	5	-	50	
$AlPO_4$	0.1	275	54	47	2.6	1	1.3	12	4
AlPON	0.1	275	48	43	2.6	1	1.3	12	
SiO_2-Al_2O_3	0.1	275	100	100	2.6	1	1.3	-	
$H_3PW_{12}O_{40}$	0.18	300	70	99	10	1	-	10	5
P-oCNT	0.1	260	94	99	1	1	0.33	60	This work

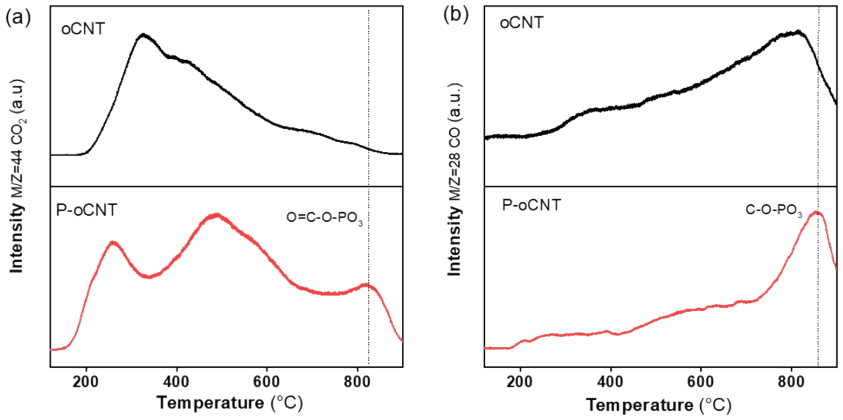

Fig. S4. Amount of CO_2 (a) and CO (b) evolved as a function of temperature during the TPD experiment for oCNT and P-oCNT before reaction (TPD condition: 75 mg catalysts, 10 mL/min He, heating rate: 5 °C min^{-1}, 120-900 °C).

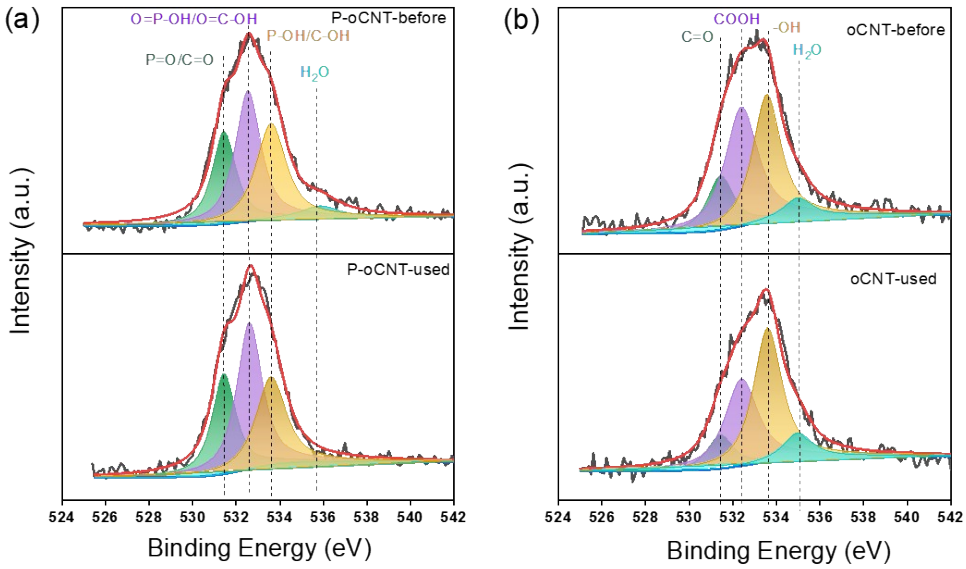

Fig. S5. O1s XPS of (a) P-oCNT and (b) oCNT before and after nB dehydration reactions.

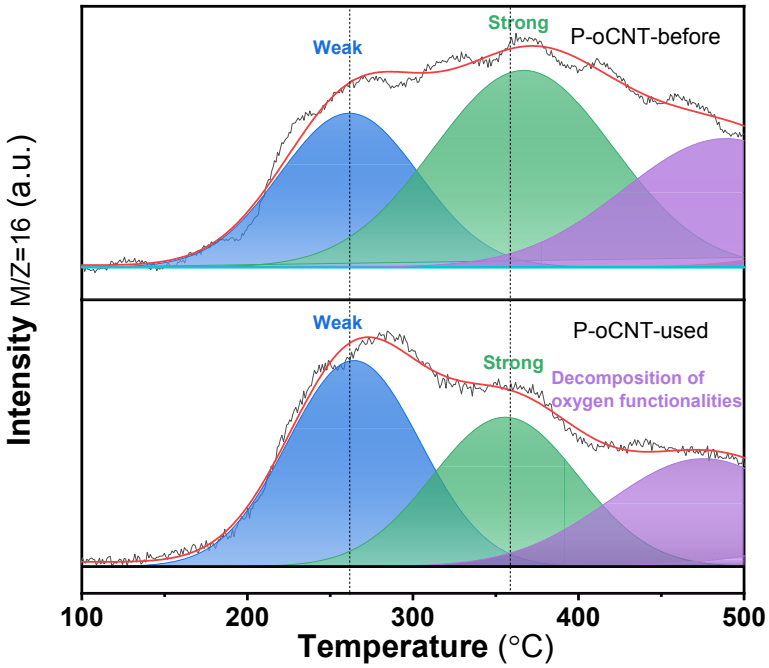

Fig. S6. NH_3-TPD profiles of P-oCNT before and after nB dehydration reactions and the corresponding peak deconvolution results.

Table S2. P 2p XPS analysis results of P-oCNT and P-SiO_2 catalysts (before and after nB conversion reactions).

Sample	P (at%)	Amount (mmol/g)	PP%	MP%	PP/MP
P-oCNT-before	1.50	1.23	35	65	0.54
P-oCNT-used	0.96	0.79	56	44	1.27
P-SiO_2-before	1.64	-	32	68	0.46
P-SiO_2-used	1.04	-	79	21	3.66

Table S3. O1s XPS analysis results of oCNT and P-oCNT catalysts (before and after nB conversion reactions).

Sample	O(at%)	C=O(P=O) %	COOH(POOH)%	C-OH(P-OH)%	H_2O%	-OOH/OH
oCNT-before	4.7	15	42	38	5	1.10
oCNT-used	3.4	11	35	46	8	0.76
P-oCNT-before	5.9	25	38	33	5	1.16
P-oCNT-used	4.8	27	42	30	0	1.41

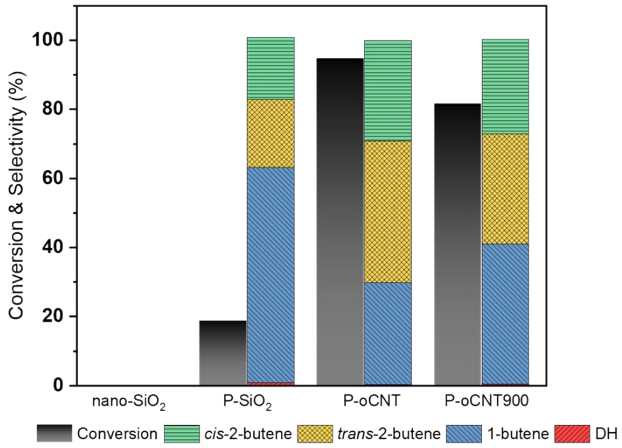

Fig. S7. Catalytic performance of different catalysts (reaction conditions: 260 °C, 1.0 kPa nB, 18 mL/min total flow rate, He balance, 100 mg catalyst).

References

1. Y. S. Hsu, Y. L. Wang and A. N. Ko, *Journal of the Chinese Chemical Society*, 2013, **56**, 314-322.
2. P. Brandão, A. Philippou, J. Rocha and M. W. Anderson, *Catalysis Letters*, 2002, **80**, 99-102.
3. A. de Reviere, T. Vandevyvere, M. K. Sabbe and A. Verberckmoes, *Catalysts*, 2020, **10**, 879.
4. S. Delsarte and P. Grange, *Applied Catalysis A: General*, 2004, **259**, 269-279.
5. C. Lang, J. Schnee, B. J. Takam Mba, F. Devred and E. M. Gaigneaux, *Catalysis Science & Technology*, 2020, **10**, 6244-6256.