Electronic Supplementary Information

Improving the Catalytic Efficiency of Carbon-Based Active Sites by Trace Oxide Promoters for Highly Productive Olefin Synthesis

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1. Starting materials and preparation of catalysts

Commercial available multi-wall carbon nanotubes were purchased from Beijing Dk Nano technology Co. LTD (ID: CNT107 50nm). 10g pristine carbon nanotubes were refluxed in 300 ml concentrated HNO_3 solution for 2 hours.Then it was filtered, washed by deionized water until pH ≈ 7, and dried at 120℃ under air overnight. The obtained refluxed carbon nanotubes was the precursor (substrate) of all the carbonaceous catalysts employed. H_3BO_3 (AR, 99%), $(NH_4)_2HPO_4$ (AR, 98.5%), NH_4VO_3 (AR, 99%), $Mn(NO_3)_2$ solution (AR, 50% wt. % in water), $Co(NO_3)_3 \cdot 6H_2O$ (AR, 99%), $Ni(NO_3)_3 \cdot 6H_2O$ (AR, 98%) and $Zn(NO_3)_3 \cdot 6H_2O$ (AR, 99%) were purchased from Aladdin Industrial Inc., and they were further diluted to 10% wt. in aqueous solution. Commercial α-Al_2O_3, TiO_2, MgO, ZrO_2 used as reference supports was purchased from Aladdin as well, whereas the MCM-41 (ordered mesoporous silica) were purchased from Nanjing XFNANO Materials Tech Co. Ltd, they were used as received without further treatment.

The OX-CNT composite catalysts were prepared via incipient wetness impregnation method by using the refluxed carbon nanotubes as support and aqueous solutions of H_3BO_3, $(NH_4)_2HPO_4$, NH_4VO_3, $Mn(NO_3)_2$, $Co(NO_3)_3 \cdot 6H_2O$, $Ni(NO_3)_3 \cdot 6H_2O$ and $Zn(NO_3)_3 \cdot 6H_2O$ as the oxide precursors. After dispersed by ultrasound for 2 h, the obtained samples were dried at 120℃ overnight, and finally calcined in helium at 500℃ for 60 min. The refluxed carbon nanotubes was also impregnated with deionized water, dried and calcined using the same process, named as CNT. Other non-CNT supported catalysts were prepared via the same incipient wetness impregnation method.

2. Physical-chemical characterization of catalysts

X-ray photoelectron spectra (XPS) were obtained with a Thermo ESCALAB 250 system with Al Kα radiation (hν = 1486.6 eV). The X-ray anode was run at 150 W. Laser Raman spectra were collected under ambient conditions using an HR LabRaman 800 system equipped with a CCD detector. A green laser beam (λ = 514.5 nm) was used for excitation. BET surface area (S_{BET}) were measured on a TriStar II 3020 V1.03 instrument at 77 K. Before the measurement, the samples were evacuated at 473 K for 2 h. The total surface area was determined by the Braunauer-Emmett-Teller (BET) method.Transmission electron microscopic (TEM) images were obtained over a JEM-2100 instrument operating at 200 kV.

3. Determination of catalytic performance

Catalytic tests were carried out in a continuous flow fixed-bed quartz tube (i.d. 7.4mm, 270mm long) at a constant total pressure (0.1 MPa). The feed gas consisted of C_3H_8 (99.9%), O_2 (99.99%) and He (99.999%), they were controlled separately by three mass flow controllers (MFC D07, Sevenstar, Beijing) to vary the total flows and the partial pressures of the reactants. The temperature of reactor was controlled by a thermocouple (sign as Tc1) placed at the center of the oven. An additional small diameter quartz tube with another thermocouple (sign as Tc2) in it was used to monitor the temperature in the inner center of the catalyst bed. The feedstock and reaction products were analyzed on-line by gas chromatography (GC-1690). Two columns were operated in parallel: a Porapak QS column (4.0 m × 1/8 in.) connected to a flame ionization detector (FID) separated and detected the organic gases, whereas a TDX-01 column (2.0 m × 1/8 in.) connected to a thermal conductivity detector (TCD) separated and detected the permanent gases (He, O_2, CO, and CO_2). Gas phase homogeneous reaction in absence of catalyst could be excluded by blank experiments. The propane conversion and the selectivity to the reaction products were calculated by the following normalization method:

$$A_{\mathrm{i}} = A_{\mathrm{i}}' \times F_{\mathrm{i}} \times v_{\mathrm{i}}$$

$$Prpane\ conversion = \frac{\sum_i A_i}{\sum_i A_i + A_{propane}} \times 100\%$$

$$Selectivity\ for\ product\ i = \frac{A_i}{\sum_i A_i} \times 100\%$$

$$yield\ for\ product\ i = \frac{\sum_i A_i}{\sum_i A_i + A_{propane}} \times 100\%$$

Where A_i is the relative quantity of the product i, A_i' is the peak area directly obtained by GC, F_i is the relative correction factor based on propane as a standard, v_i is the carbon number of reactants or products.

4. Details for kinetic catalytic testing

The kinetic data of all catalysts were measured in differential conditions. 3-400mg (depending on the intrinsic catalytic activity of the catalysts) catalyst mixed with 1000mg deactivated quartz sand (mesh number: 80-100) was placed in the reactor for the reaction test. Propane conversions were typically less than 1.3%, the difference between temperatures measured by the above-mentioned two thermocouples (Tc1 and Tc2) was less than 1℃, therefore concentration gradients of the reactant and temperature gradient of the catalyst bed were negligible.

The specific rates of propylene formation (ODH Rate) were obtained from the equations:

$$ODH\ Rate\,(\mathrm{mmol\,g^{-1}\,h^{-1}}) = \frac{C_3H_6\ Yield \times D}{m_{catalyst}}$$

$$ODH\ Rate\,(\mathrm{mmol\,m^{-2}\,h^{-1}}) = \frac{C_3H_6\ Yield \times D}{S_{SP(catalyst)} \times m_{catalyst}}$$

Where $S_{SP(catalyst)}$ is the specific surface area of the catalyst (m^2 g^{-1}), $m_{catalyst}$ is the mass of catalyst, D is the propane flow (mmol h^{-1}).

The Arrhenius equation enable the determination of apparent activation energies and the apparent pre-exponential factor:

$$ODH\ Rate = A_{app} \times e^{-\frac{E_a}{RT}}\ ODH\ Rate = A_{app} \times e^{-\frac{E_a}{RT}}$$

The reaction was first performed at the highest temperature (373℃/646 K) for 8 h, and the apparent activation energy was determined by step-wise cooling (10 K steps) down to 606 K. Two or three separate GC samples were taken and averaged for each experimental data point.

5. Figures

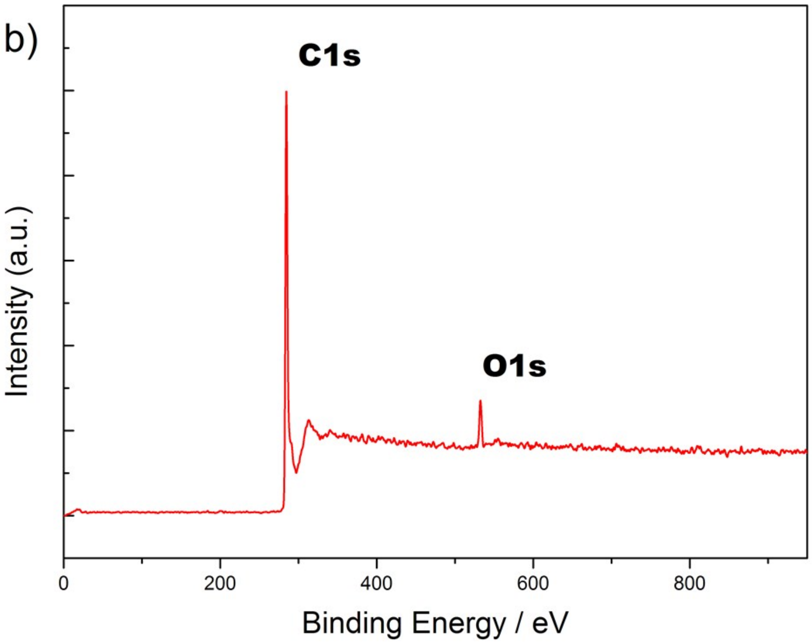

Fig. S1 Full survey XPS curve of the CNT substrate, two peaks centred at 284.5 and 532 eV were corresponding to C1s and O1s, respectively, and there was no signal of metallic catalysts or any other elements in the CNT surface at the limit of detection.

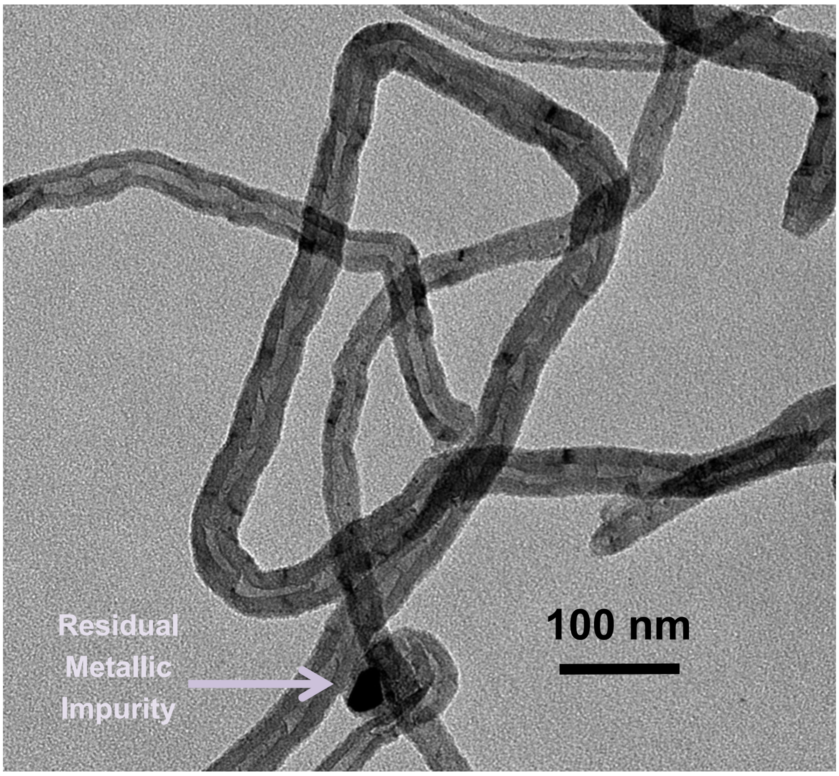

Fig. S2 TEM image of the CNT substrate. Purification by refluxing in nitric acid can effectively removed the residual metallic impurities on CNT surface to a great extent, and the remaining impurities were mainly sheathed by several graphene sheets and not exposed to the reactants.[1,2]

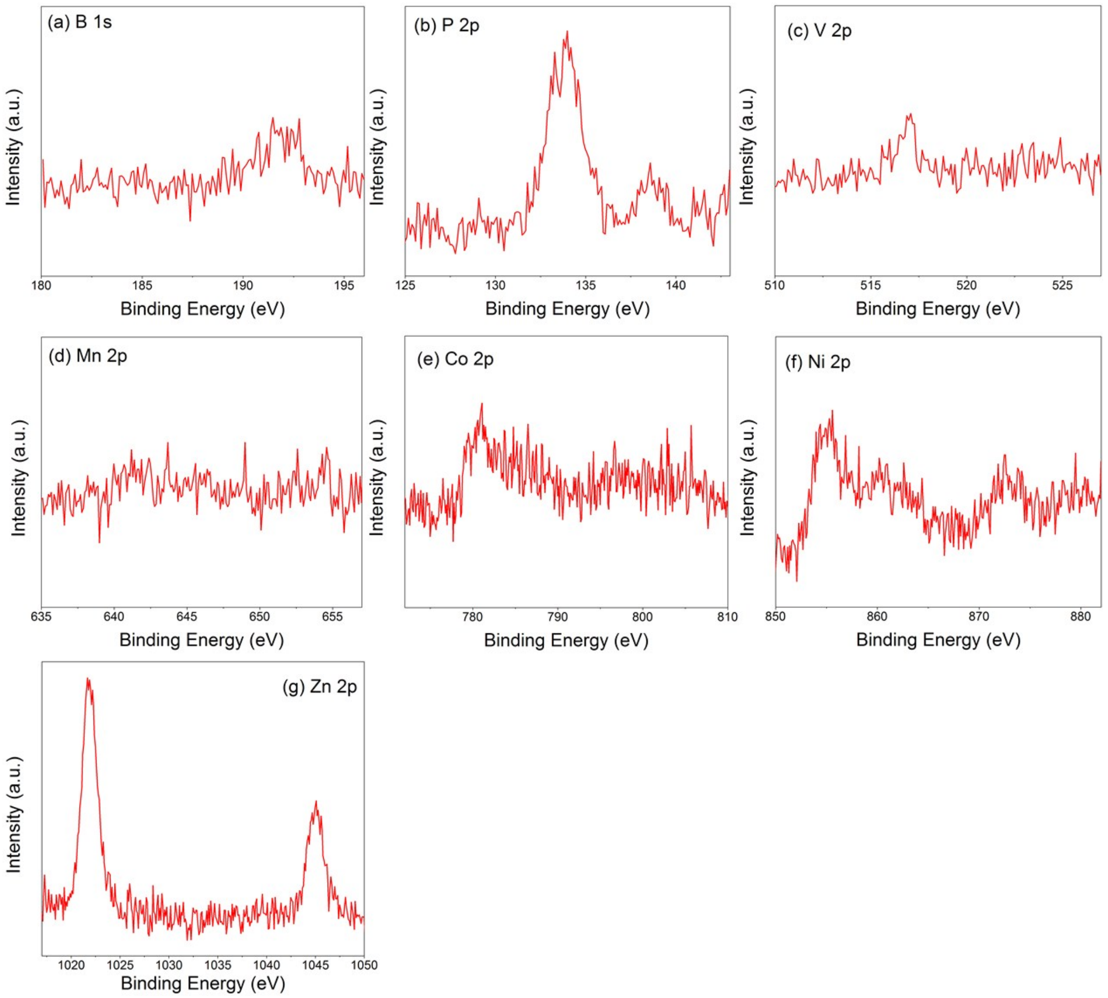

Fig. S3 XPS profiles of heteroatoms of various OX-CNT samples: a) B 1s spectra of BO_x-CNT; b) P 2p spectra of PO_x-CNT; c) V 2p spectra of VO_x-CNT; d) Mn 2p spectra of MnO_x-CNT; e) Co 2p spectra of CoO_x-CNT; f) Ni 2p spectra of NiO_x-CNT; g) Zn 2p spectra of ZnO_x-CNT.

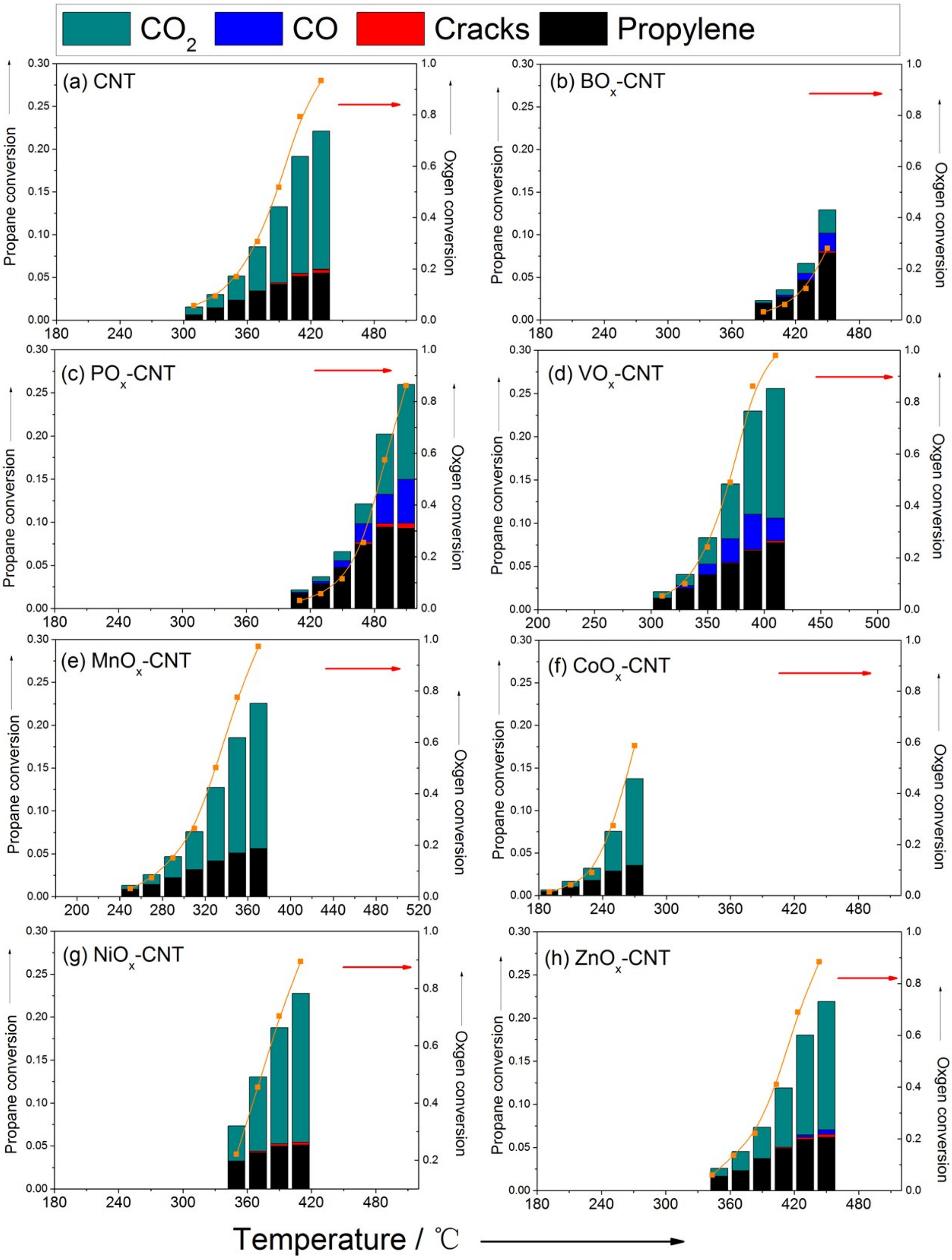

Fig. S4 Propane conversion (columns) and oxygen conversion (dots) as a function of reaction temperature on CNT and OX-CNT samples. Reaction conditions: 16.6% C_3H_8, 15% O_2, and 68.4% He; overall flow velocity = 18 ml min^{-1}; 200mg catalysts. It should be noted that propene selectivity at the same conversion tend to increase with the reaction temperature.

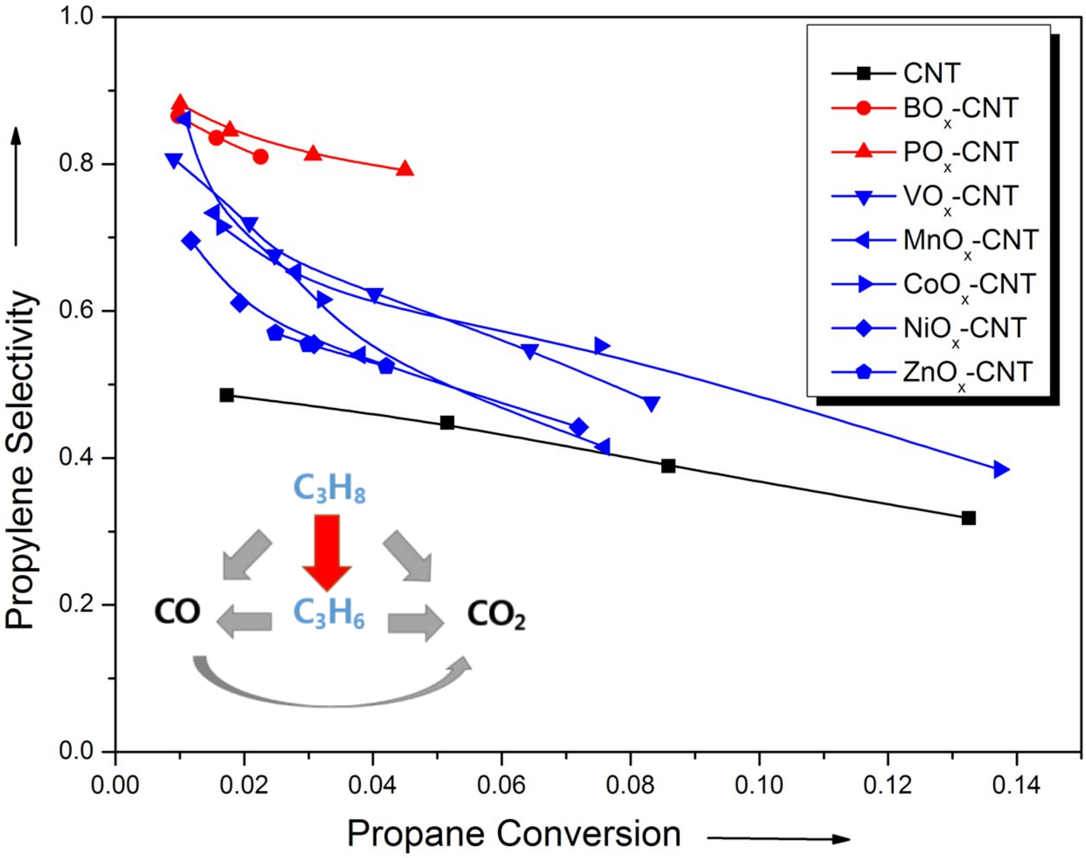

Fig. S5 Propylene selectivity as a function of propane conversion. Reaction conditions: 400℃ (BO$_x$- and PO$_x$-CNT), 350℃ (other catalysts); 16.6% C_3H_8, 15 % O_2, and 68.3% He; overall flow velocity = 18 ml min^{-1}; 5-500mg catalysts.

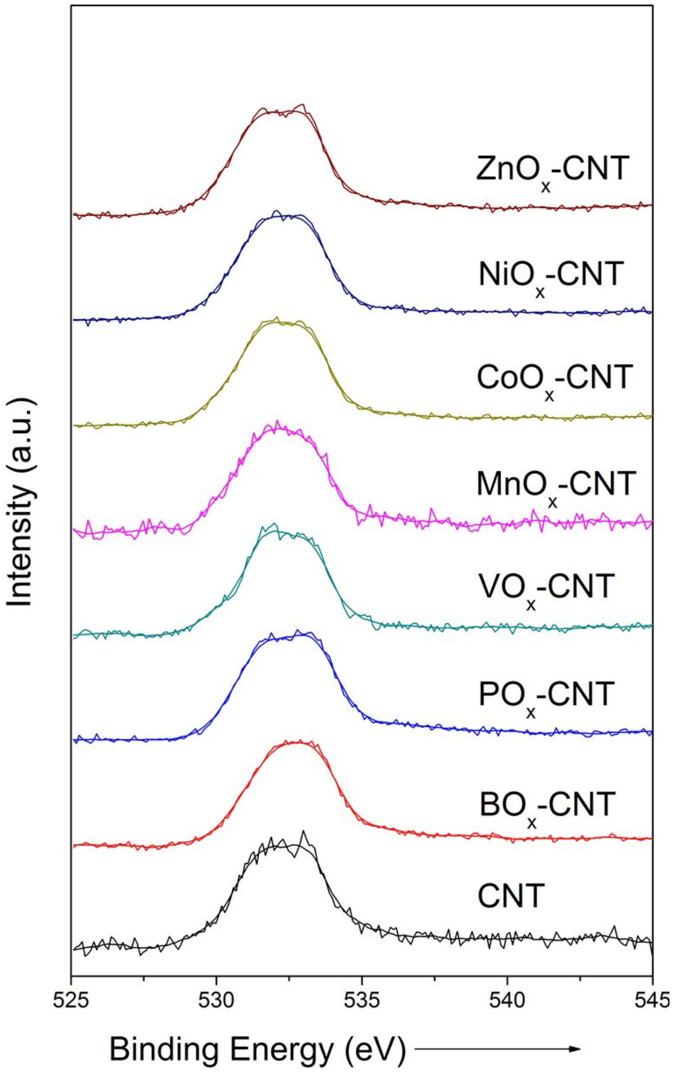

Fig. S6 XPS profiles of O1s spectra of different OX-CNT samples.

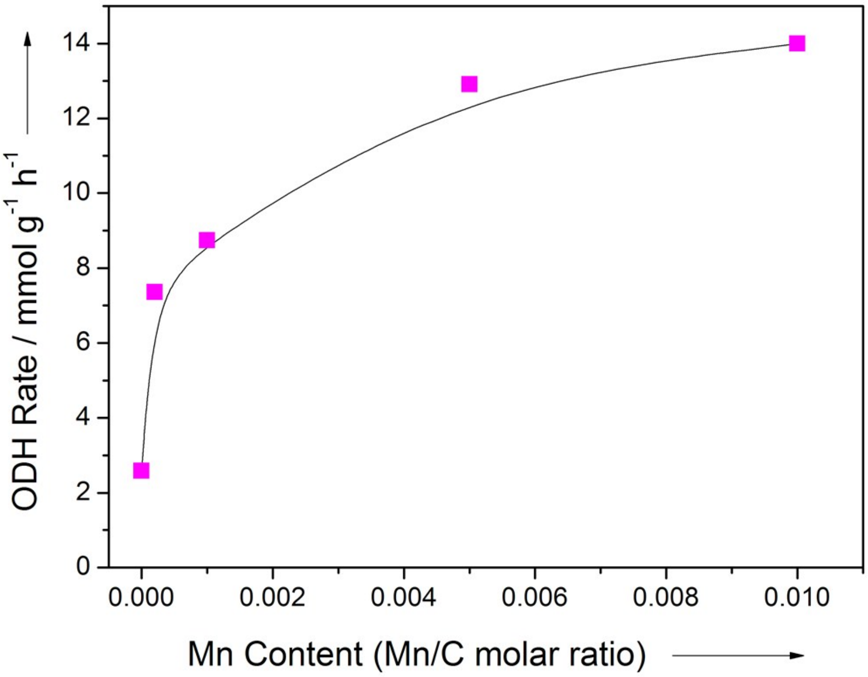

Fig. S7 Catalytic propane ODH rate as a function of Mn content. Reaction conditions: 353°C; $C_3H_8/O_2/He=1/1/4$; overall flow velocity = 30 ml min^{-1}.

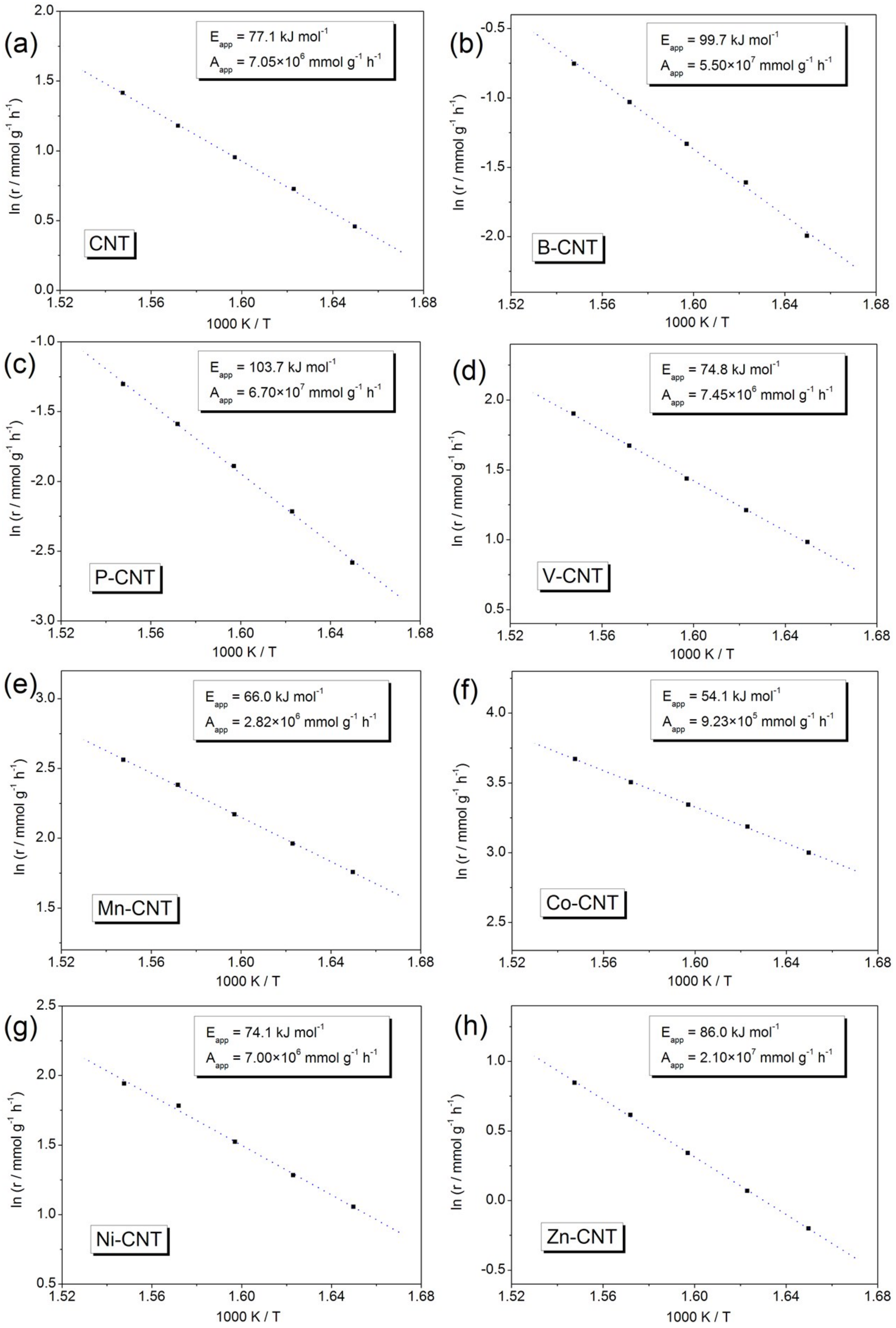

Fig. S8 (a) - (e) Experimental Arrhenius relationship (temperature dependencies of intrinsic activities) for ODH reaction catalyzed by CNT and various OX-CNT samples. The obtained kinetic parameters were listed in the top right corner.

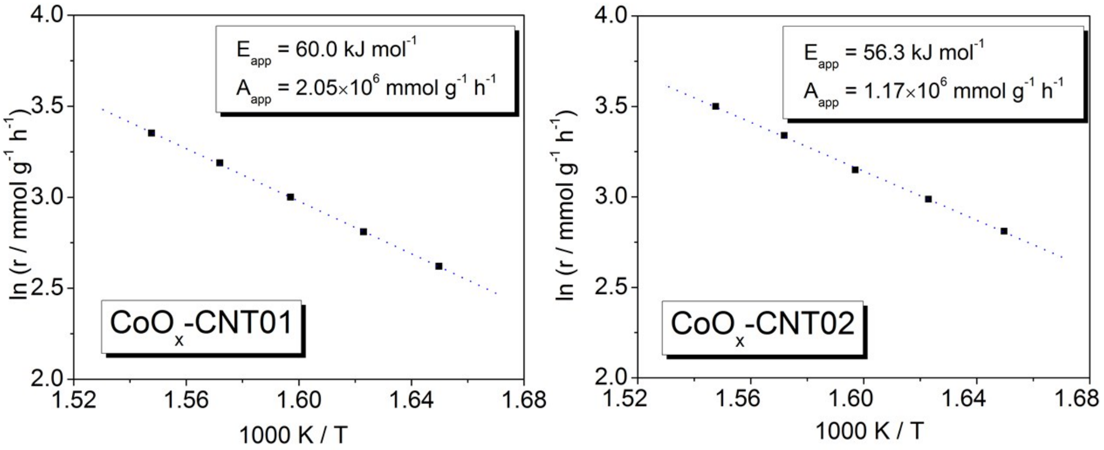

Fig. S9 Experimental Arrhenius relationship for ODH reaction catalyzed by two more OX-CNT samples with lower Co loading.

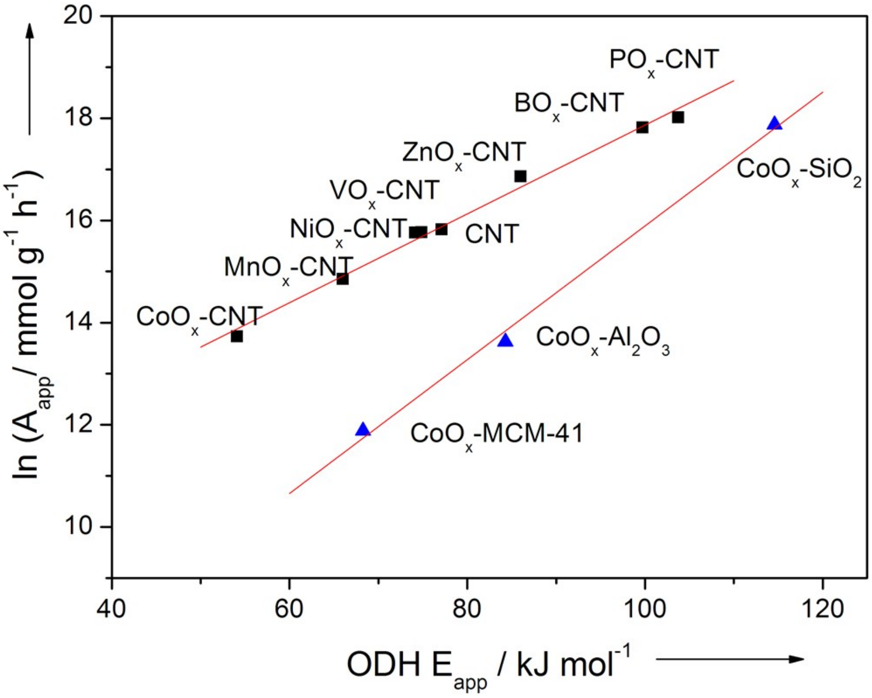

Fig. S10 The compensation relationship between ln A_{app} and ODH apparent activated energy.

6. Tables

Table S1. Catalytic performance of some propane ODH catalysts in the recent literature.

Ref.	Catalyst	T / ℃	W/F g s ml^{-1}	C$_3$H$_8$ content	O$_2$ content	Conversion	C$_3$H$_6$ selectivity	C$_3$H$_6$ STY/ kg kg$_{cat}^{-1}$ h^{-1}
This work	CoO$_x$-CNT	370	0.016	16.6%	3.3%	2.5%	72%	1.1
		370	0.016	16.6%	16.6%	3.9%	63%	1.5
3	RGO-2%ND (Graphene-Nano diamond composite)	400	n.d.[a]	15%	5%	n.d.	69%	0.29
4	NCNT-1 (N-Doped CNT)	400	0.02	5%	5%	0.41%	61%	0.044
5	NO$_2$-treated CNT	400	n.d.	8.3%	8.3%	n.d.	45%	0.105
6	MnWO$_4$	400	1.8	10%	5%	8%	40%	0.013
7	4V-18Ta	490	n.d.	30%	15%	3.5%	82%	1.2
8	V/TiSBA15[b]	500	n.d.	28.6%	17.3%	n.d.	n.d.	8.5

[a] n.d. = not determined. [b] Propylene productivity obtained on the V/TiSBA15 at 500 °C was the maximum reported.

The catalysts listed were demonstrated to have superiority in low-temperature (≦500℃) productivity (activity). A survey of literature from Cavani et al. showed that the STY obtained on the majority of previously studied ODH catalysts could hardly reach the recognized industrial targets (at least 1 kg kg$_{cat}^{-1}$ h^{-1}) even at temperature higher than 600°C.[9]

7. References

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