

## Electronic supplementary information

### **Niobium oxide promoted by alkali metal nitrates for soot particulate combustion: Elucidating the vital role of active surface nitrate groups**

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## 1. Supplementary Experimental

### 1.1 Catalyst characterization

The Powder X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8Focus diffractometer instrument operating at 40 kV and 30 mA, with Cu target  $K\alpha$ -ray irradiation ( $\lambda = 1.5405 \text{ \AA}$ ). Scans were taken with a  $2\theta$  range from  $10\text{--}90^\circ$  and with a step of  $2^\circ \text{ min}^{-1}$ . To keep the data comparable, all of the samples were tested continuously.

Raman spectra of the catalysts were recorded on a Renishaw in Via Raman spectrometer equipped with an argon laser excitation source operating at 532 nm and a Renishaw Ren Cam CCD detector. The scanned Raman shift range is from 200 to 1400  $\text{cm}^{-1}$ .

TGA was recorded on a Mettler Toledo TGA-DSC3+ instrument with a heating rate of  $10^\circ \text{C min}^{-1}$  from room temperature to  $800^\circ \text{C}$  in an air flow of  $20 \text{ mL min}^{-1}$ .

The presence of nitrate anions on fresh and used catalysts was studied by means of FTIR spectroscopy using a Thermo Scientific Nicolet iS10 equipment. Spectra were recorded at room temperature in the range of  $4000\text{--}400 \text{ cm}^{-1}$  and the samples were prepared in form of discs with KBr.

$\text{H}_2$ -TPR experiments were carried out on FINESORB 3010C instrument. Generally, 0.05 g catalysts were used for the tests. Before the experiments, the catalysts were pretreated in a high purity air flow at  $120^\circ \text{C}$  for 30 min to remove any possible surface impurities. After purging with an ultra-high purity Ar flow at room temperature for 30 min, the temperature was then increased from room temperature to  $800^\circ \text{C}$  with a ramp of  $10^\circ \text{C min}^{-1}$  in a  $30 \text{ mL min}^{-1}$  10%  $\text{H}_2/\text{Ar}$  gas mixture flow. A thermal conductivity detector (TCD) was employed to monitor the  $\text{H}_2$  uptake. To quantify the  $\text{H}_2$  consumption amount, a 99.99% CuO sample was used as the calibration standard.

Elemental phase mapping and surface scans were obtained by energy-dispersive spectroscopy (EDX) using the Tecnai<sup>TM</sup> F30 microscope equipped with an Oxford EDX detector operated at 300 keV.

$\text{O}_2$ -TPD measurements were carried out on the AutoChem 2920 multiple adsorption instrument equipped with a TCD detector. Typically, 0.05 g sample was placed in a

quartz reactor, which was pretreated in a 30 mL min<sup>-1</sup> ultra-high purity He flow at 400 °C for 60 min. Afterwards, the sample was cooled down to 50 °C and saturated in a 3% O<sub>2</sub>+He flow with a rate of 30 mL min<sup>-1</sup>, which was followed by flushing in a 30 mL min<sup>-1</sup> ultra-high purity He flow for 60 min to remove any physically adsorbed O<sub>2</sub>. O<sub>2</sub>-TPD experiments were then carried out from 50 °C to 800 °C with a heating rate of 10 °C min<sup>-1</sup> in a 30 mL min<sup>-1</sup> ultra-high purity He flow.

Soot-TPR experiments were conducted using a DAS-7000 multiple adsorption instrument (HUASI, China). Typically, 55 mg sample, which was prepared by the uniform mixing of 5 mg soot and 50 mg catalyst powder, was placed in a quartz reactor. Prior to the test, it was treated in an ultra-high purity He flow for 60 minutes at 120 °C to remove any physically adsorbed impurities. Afterwards, soot-TPR was carried out from 50 to 550 °C with a heating rate of 10 °C min<sup>-1</sup> in a 30 mL min<sup>-1</sup> ultra-high purity He flow.

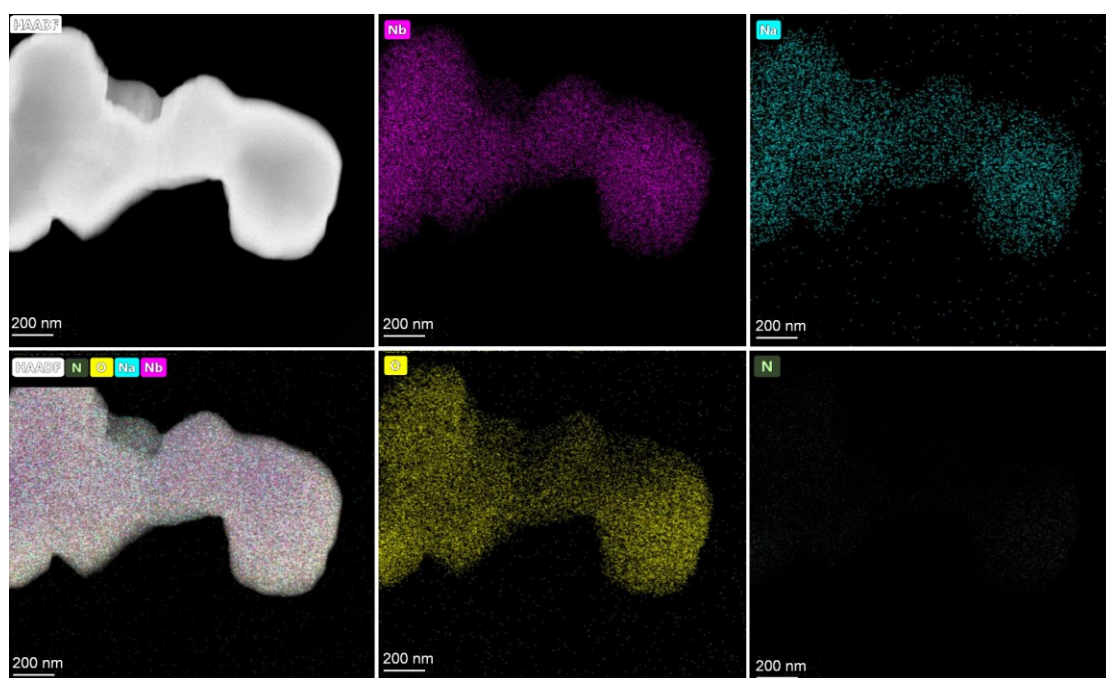
The QMS-1800 mass spectrometer (Finetec, China) was used to detect the products. The mass spectrum signal  $m/z=32$  was used to detect the generation of O<sub>2</sub>, and  $m/z=30$  is used to detect the generation of NO .

## 1.2 Activity evaluation

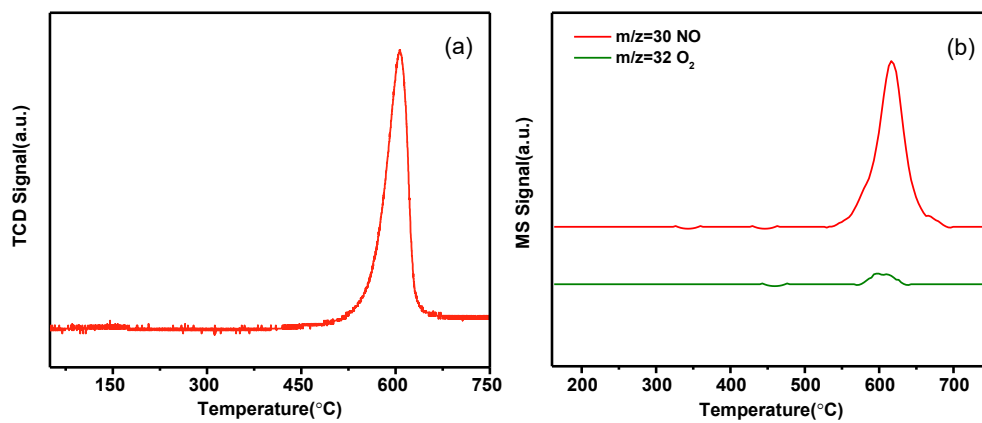
Temperature programmed oxidation technique (TPO) was used to evaluate the activity of the prepared catalysts for soot combustion. Tests were carried out in a fixed-bed quartz tube micro-reactor with an inner diameter of 6 mm. To evaluate the activity of a catalyst under tight contact condition, typically, 5 mg soot (Printex-U, diameter of 25 nm, purchased from Degussa) was mixed with 50 mg catalyst powder and grounded for 10 min (To evaluate the activity of a catalyst under loose contact condition, typically, 5 mg soot was mixed with 50 mg catalyst powder and mixed for 3 min). Before loading into the reactor, the grounded mixture was diluted by 100 mg inert silica with a soot/catalyst/silica weight ratio of 1/10/20 to avoid the formation of hot spots during the activity test. A K-type thermocouple was used to monitor the temperature of the catalyst bed accurately with the thermocouple head point touching the catalyst bed. To measure the reaction behaviors of the catalysts, all data were collected with the increasing of the temperature to 800 °C at a rate of 10 °C min<sup>-1</sup>. The volume

composition of the feed gas is 10% O<sub>2</sub> and balanced by high purity Ar, with a flow rate of 30 ml min<sup>-1</sup>. To accurately quantify the O<sub>2</sub> consumption amount, prior to entering the TCD, the formed CO<sub>2</sub> was removed thoroughly by a Soda-lime trap. The catalytic activity was evaluated by the ignition temperature (T<sub>i</sub>), highest combustion rate temperature (T<sub>p</sub>) and complete combustion temperature (T<sub>c</sub>) reflected in the TPO profiles, respectively. To identify the product selectivity, the soot combustion reaction was also monitored by an on-line SHP8400PMS mass spectrometry (MS) without using a Soda-lime trap. The m/z = 44 signal is used to monitor the amount of CO<sub>2</sub>. By subtracting the m/z = 28 fragment of CO<sub>2</sub>, this signal is used to monitor the amount of CO. The CO<sub>2</sub> selectivity (S<sub>CO2</sub>) is obtained according to the equation:  $S_{CO2} = C_{CO2} / (C_{CO} + C_{CO2})$ . C<sub>CO2</sub> and C<sub>CO</sub> are the outlet concentrations of CO<sub>2</sub> and CO, respectively.

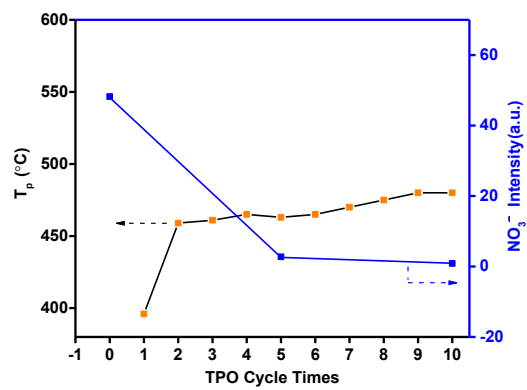
## 2. Supplementary results



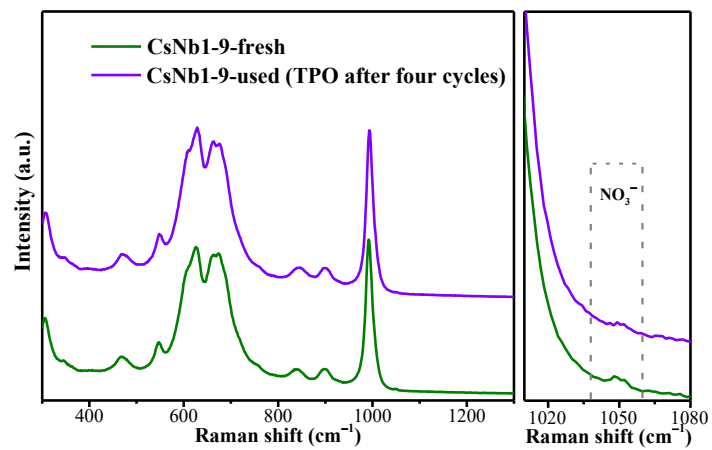
**Fig. S1.** STEM-mapping images of NaNb<sub>1-9</sub> catalyst.



**Fig. S2.** O<sub>2</sub>-TPD experiment performed on CsNb<sub>1-9</sub> catalyst with an on-line, (a) TCD detector, (b) mass spectrometry detector



**Fig. S3.** Stability tests of CsNb1-9 catalyst with 10 consecutive cycles



**Fig. S4.** Raman spectra of CsNb1-9 catalyst.