Electronic Supplementary Information

Doping SnO$_2$ with metal ions of varying valence states: discerning the importance of active surface oxygen species *vs.* acid sites for C$_3$H$_8$ and CO oxidation

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1. Supplementary Experimental

1.1. Catalyst preparation

All the chemicals are commercialized products. SnC2O4 (AR) , Cr(NO$_3$)$_3$·9H$_2$O (AR), C$_{10}$H$_5$NbO$_{20}$·xH$_2$O (AR), Zr(NO$_3$)$_4$·5H$_2$O (AR) are provided by Aladdin Industrial Corporation (Shanghai, China). Mg(NO$_3$)$_2$·6H$_2$O, LiNO$_3$, Citric acid is provided by Xilong Chemical Company (Guangdong, China).

SnC$_2$O$_4$ was dissolved with a certain amount of DDI water and heated in a water bath at 80 °C. Afterward, H$_2$O$_2$ (30%) was dripped slowly into the solution until a clear solution was formed. Afterwards, the corresponding doping chemicals, such as LiNO$_3$, Mg(NO$_3$)$_2$·6H$_2$O, Cr(NO$_3$)$_3$·9H$_2$O, Zr(NO$_3$)$_4$·5H$_2$O, C$_{10}$H$_5$NbO$_{20}$·xH$_2$O, with a Sn/M molar ratio of 9/1 were added to form aqueous solutions and continuously stirring for 1 h. Citric acid equaling to 1.2 times of the total molar amount of metal cations was then added into the solution mixtures under constant stirring, and heated at 80 °C to get

a transparent gelatin. The gelatin was dried overnight in an oven at 110 °C, which was then calcined in air with a heating ramp of 2 °C min^{-1} to 500 °C, and remained for 4 h to obtain the finalized catalysts. The catalysts were named M-SnO$_2$ (M= Li, Mg, Cr, Zr, Nb) according to the chemical compositions. For comparison, a pure SnO$_2$ sample was also prepared by the same method.

1.2. Activity evaluation

The samples were evaluated for CO oxidation with a fixed bed reactor. The volume composition of the feed gas is 1% CO, 21% O$_2$ and balanced by N$_2$, with a total flow rate of 30 mL min^{-1}. Generally, 0.09g sample was used for activity evaluation, which resulted in a WHSV of 20000 mL g^{-1}·h^{-1}. A K-type thermocouple was placed on top of the catalyst bed with the head point touching the sample to monitor the accurate reaction temperatures. To measure the light-off behaviors of the catalysts, all data were collected by increasing the temperature. The reactants and products were analyzed on-line on a GC9310 gas chromatograph equipped with a TDX-01 column and a TCD detector. Before analysis, the reaction at each temperature over the catalysts was stabilized at least 30 min.

The oxidation of Propane over the catalysts was evaluated using a quartz tube (ID = 6 mm) reactor with a continuous flow over 0.09g catalyst mixed the same weight silica sand. A K-type thermocouple was placed in the catalyst bed with the thermocouple head point touching the catalyst to monitor the reaction temperatures. To measure the light-off behavior of the catalysts, all the data were collected on 0.09 g of catalyst by increasing the temperature. The volume composition of the feed gas was 5000 ppm Propane/21% O$_2$ and balanced by high purity N$_2$. The flow rates of the feed gases were 30 mL/min, which resulted in GHSV = 20000 mL h^{-1} g^{-1} for Propane oxidation. The reactants and products were analyzed on-line on a GC9310 gas Chromatograph equipped with a TDX-01 column and a TCD detector. Before analysis, the reaction at each temperature point over the catalyst was stabilized for 30 min to obtain steady state reaction.

1.3 Catalyst characterization

The Powder X-ray diffraction (XRD) was carried out on an X-ray diffractometer manufactured by Beijing Puji, with a tube voltage of 40 kV and a tube current of 30 mA, using a CuKα radiation source. The scanning 2θ range is 10 ° - 80 °, and the scanning step is 2 ° min^{-1}.

X-ray Photoelectron Spectroscopy (XPS) tests were performed with a PerkinElmer PHI1600 system using a single MgKα X-ray source operated at 300 W and 15 kV voltage. The spectra were collected at room temperature with an ultra-high vacuum. The binding energies were calibrated by using the C 1s peak of graphite at 284.6 eV as a standard.

EPR technique has been used to measure the catalysts. The catalysts were pretreated in 100 Torr oxygen at 750 ^{o}C for 1 h and then cooled down to room temperature, which was followed by evacuation and then placed in liquid nitrogen of 77K prior to record the EPR signals. Afterwards, the EPR spectra were recorded with a JEOL FA-200 EPR Spectrometer, operating with a field modulation of 100 kHz and microwave frequencies of 9067.558 MHz.

The specific surface areas of the samples were measured by N_2 adsorption-desorption at 77 K on an ST-08B instrument.

ICP experiments were conducted on Agilent 700 system to verify the element compositions of the catalysts.

Raman spectra of the catalysts were measured using an excitation wavelength of 532 nm in Renishaw in Via instrument equipped with an argon laser excitation source. The scanned Raman shift range is from 100 to 1400 $cm^{-1.}$

Hydrogen temperature programmed reduction (H_2-TPR) was performed on the FINESORB 3010C automatic temperature programmed chemical adsorption instrument of Zhejiang Fantai. The amount of catalyst used in the test was 50 mg. First, the catalyst was pretreated in the Ar atmosphere at 120 ° C for 30 min and then cooled to room temperature. The treatment gas is switched to a 10% H_2/Ar mixture. After the baseline is stabilized, the catalyst bed is raised from room temperature to 800 °C at a

heating rate of 10 °C min^{-1}, and the tail gas enters the thermal conductivity detector (TCD) to test and record the results of the experiment.

Propane temperature programmed desorption (Propane-TPD) and NH$_3$ temperature programmed desorption (NH$_3$-TPD) was performed on the DAS-7000 temperature programmed chemical adsorption instrument of HUASI. Typically, 50 mg catalyst was pretreated in a 30 mL/min high purity Ar flow at 400 °C 1h to remove any possible impurities and H$_2$O. Afterwards, the sample was cooled to 50 °C and adsorb feed gas for 1h was followed by purging with a 30 mL/min 99.99% Ar flow to remove any physically absorbed molecular for 30 min. After all these pretreatments, the catalyst was heated from 50 to 800 °C with a rate of 10 °C/min. A TCD was employed to monitor the desorption gas.

O$_2$ temperature programmed desorption (O$_2$-TPD) was performed with a micromeritics Auto Chem 2920 apparatus. Typically, 50 mg catalyst was pretreated in a 30 mL/min high purity He flow at 550 °C for 1h to remove any possible impurities and carbonate. Afterwards, the sample was cooled to 50 °C and was followed by purging with a 30 mL/min 99.99% He flow to remove any physically absorbed O$_2$ for 30 min. After all these pretreatments, the catalyst was heated from 50 to 800 °C with a rate of 10 °C/min. A TCD was employed to monitor the O$_2$ desorption. The O$_2$ desorption amount of the catalysts were quantified by using a KMnO$_4$ (99.9%) standard, which decomposes completely around 600 °C according to the stoichiometry expressed by the equation of $2KMnO_4 = K_2MnO_4 + MnO_2 + O_2\uparrow$.

In Situ DRIFTS experiments were carried on a Bruker Vertex equipped with an MCT detector chilled in liquid nitrogen. A micro-size *In Situ* DRIFTS furnace equipped with KBr windows was used. 100 mg powder sample was pretreated at 500 °C for 60 min in a high purity 30 mL min^{-1} Ar flow and then cooled target temperature. At this stage, the background spectra were collected at a resolution of 4 cm^{-1} by accumulating 64 scans in a 30 mL/min Ar flow. All the spectra exhibited in this study were achieved by subtracting the corresponding background spectrum. The spectra were recorded continuously for each series of in situ experiments until the reaction reached equilibrium, which is about 2 min.
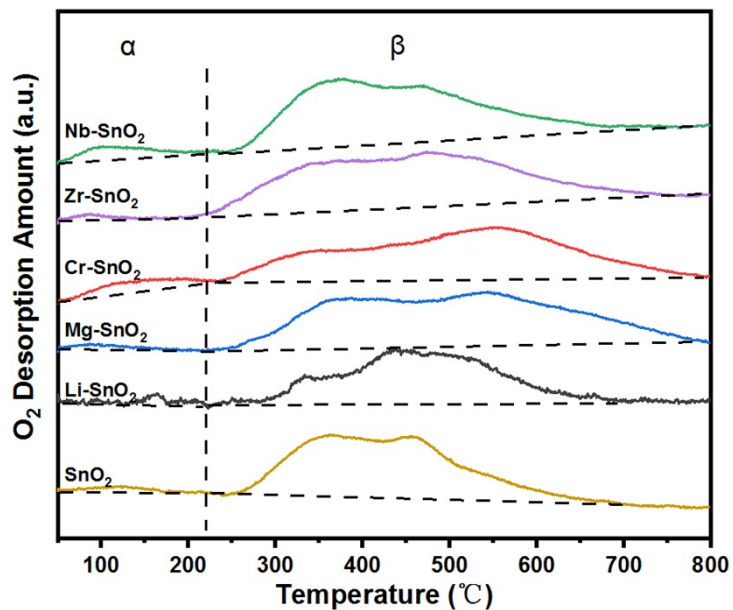
2. Supplementary Results

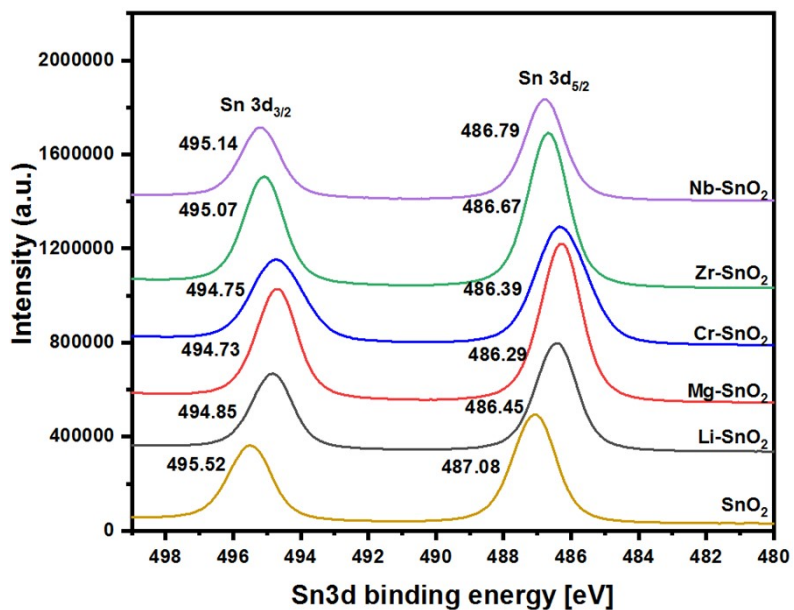**Fig. S1.** O_2-TPD profiles of the catalysts.

Fig. S2. XPS Sn 3d spectra of the catalysts.

Fig. S3. XPS spectra of the catalysts. (a) Li 1s; (b) Mg 1s; (c) Cr 2p; (d) Zr 3d; (e) Nb 3d.

Table S1 XPS quantification results of the catalysts

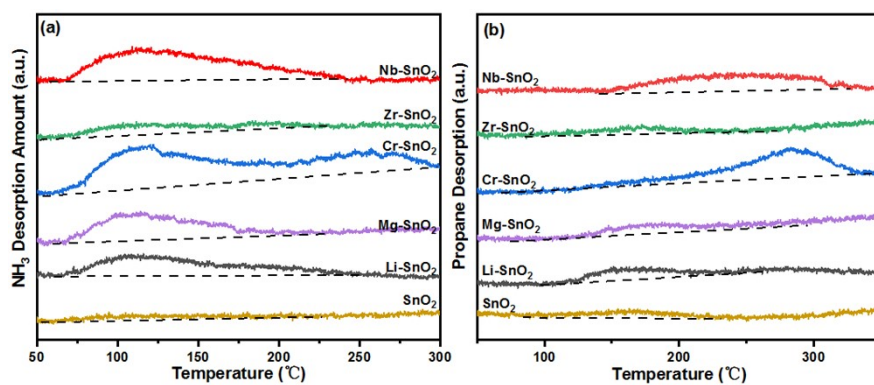| Samples	O 1s binding energy (eV)		O_2^-/O^{2-} ratio	Sn 3d binding energy (eV)		ΔE (eV)	Sn/M molar ratio
	O^{2-}	O_2^-		Sn 3d$_{3/2}$	Sn 3d$_{5/2}$		
SnO$_2$	531.00	533.36	0.021	495.52	487.08	8.44	-
Li-SnO$_2$	530.33	533.17	0.011	494.85	486.45	8.40	6.9/1
Mg-SnO$_2$	530.15	532.73	0.017	494.73	486.29	8.44	6.5/1
Cr-SnO$_2$	530.04	533.25	0.058	494.75	486.39	8.36	7.9/1
Zr-SnO$_2$	530.54	532.80	0.022	495.07	486.67	8.40	8.6/1
Nb-SnO$_2$	530.54	533.10	0.068	495.14	486.79	8.24	7.4/1

Fig. S4. (a) NH$_3$-TPD; (b) Propane-TPD profiles of the catalysts.
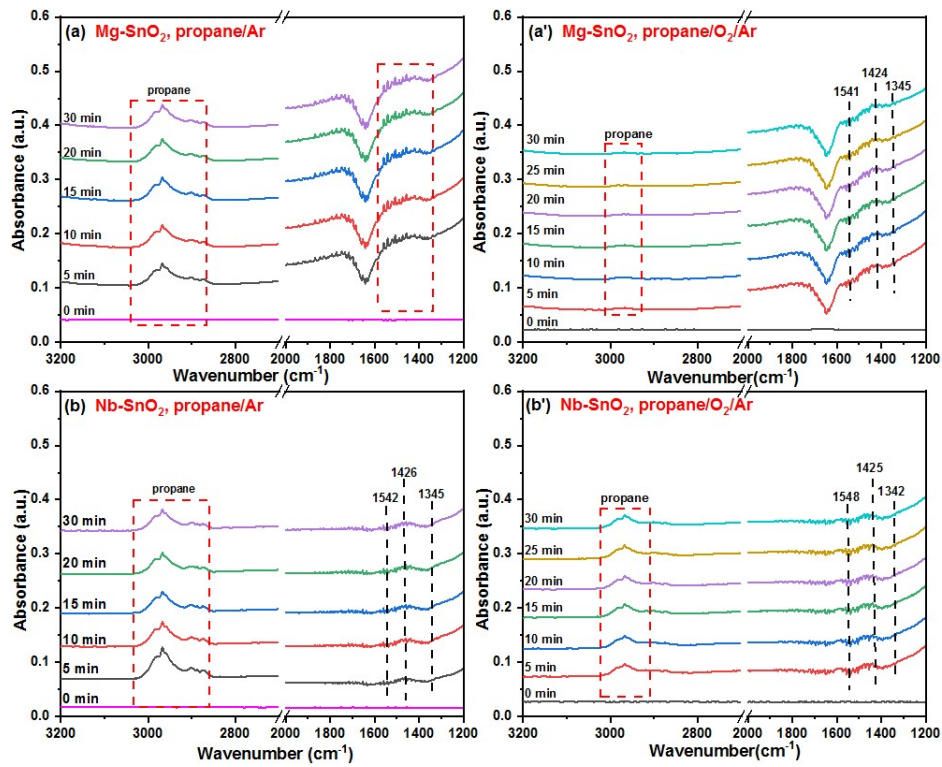
Fig. S5. In situ DRIFTS experiments on M-SnO$_2$ performed at 300 $^\circ$C. (a, b) exposed in a propane/Ar flow, (a′, b′) exposed in the reaction feed of 5000 ppm propane/10 % O$_2$/Ar.
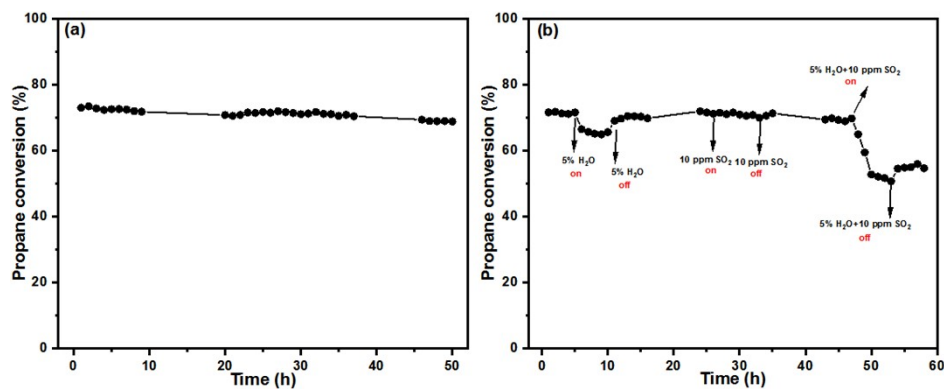

Fig. S6. Stability of Cr-SnO$_2$ for 50 h at 320 $^\circ$C.
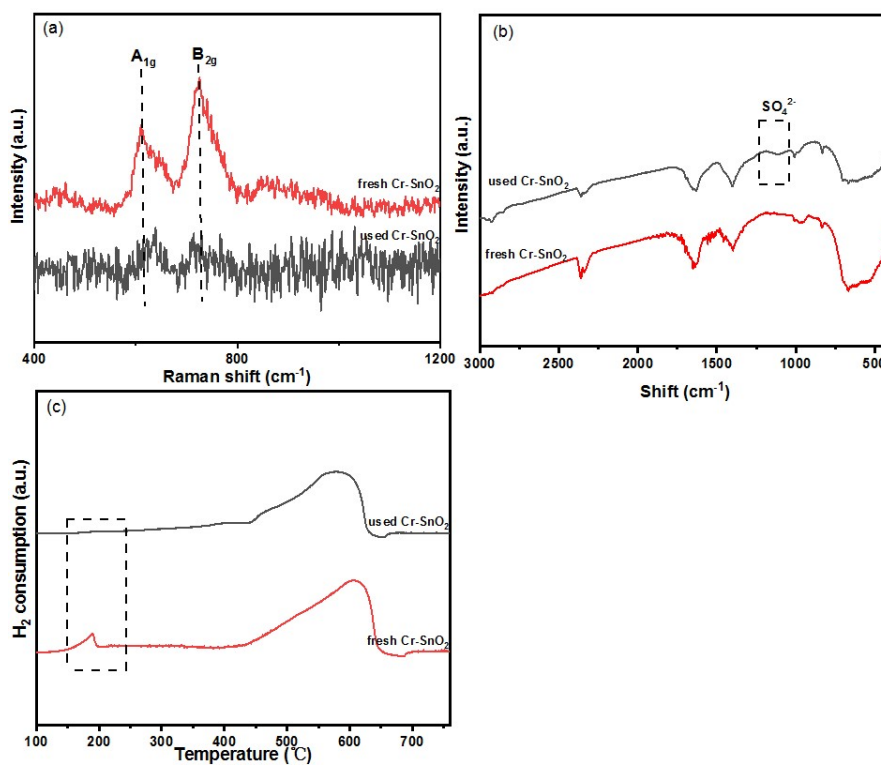
Fig. S7. Characterization of the fresh and used Cr-SnO$_2$ catalysts. (a) Raman spectra; (b) FTIR spectra; (c) H$_2$-TPR profiles.