Supporting Information

Tailoring Active O_2^- And O_2^{2-} Anions on ZnO Surface with the Addition of Different Alkali Metals Probed by CO Oxidation

Yue Sun [a], Junwei Xu [a], Xianglan Xu [a], Xiuzhong Fang [a], Yao Guo [a], Rui Liu [a], Wei Zhong [b], Xiang Wang [a,]*

[a] *Key Laboratory of Jiangxi Province for Environment and Energy Catalysis, College of Chemistry, Nanchang University, Nanchang, Jiangxi, 330031, China*

[b] *College of Biological, Chemical Sciences and Engineering, Jiaxing University, Jiaxing, Zhejiang 314001, China*

[*] *Corresponding Author，E-mail*: xwang23@ncu.edu.cn (X. Wang)

1. Supplementary Experimental Information

1.1 Catalyst Preparation

The samples were prepared by citric acid assisted sol-gel method reported previously[1], but with some appropriate modification. In detail, 8g $Zn(NO_3)_2 \cdot 6H_2O$ (analytical pure) and an appropriate amount of MNO_3 (M=Li, Na, K, Cs) (analytical pure) were dissolved together into 50 ml deionized distilled (DDI) water to form a stable and transparent solution with a Zn/M atomic ratio of 0.95:0.05. Then, citric acid (analytical pure) was add into the solution with a molar ratio of citric acid/(Zn+M) = 2/1 to get a uniform solution, which was then heated in a water bath at 80 ℃ until a

yellow gel was obtained, and followed by further drying in an oven at 110 ℃ overnight. Afterwards, the gel was calcined first at a relatively mild temperature of 300 ℃ in air atmosphere in a muffle oven for 30 min separately to avoid sudden ignition and contamination to each other. After this step, all the samples were calcined together in air atmosphere in a muffle oven with a heating ramp of 2 ℃/min from room temperature to 500 ℃, and kept at the same temperature for 4 hours to obtain the final catalysts. According to the compositions, the final catalysts are named Li-ZnO, Na-ZnO, K-ZnO and Cs-ZnO, respectively. As listed in Table 1, the element compositions of the catalysts have been confirmed by ICP analysis, which is the same to the original ratios adopted for sample preparations within the experimental. Notably, pure ZnO was also prepared with the same method for a comparison study.

1.2 Catalyst characterization

XRD patterns were collected on a Beijing Puxi XD-2 Focus diffractometer using a Cu target and Kα X-ray irradiation, which is operated at 40KV and 30mA. Scans were collected over a 2θ range from 10° to 90° with a step of $2°\cdot min^{-1}$.

Raman spectra were obtained on a Renishaw inVia Raman spectrometer equipped with an argon laser excitation source operating at 532 nm and a Renishaw RenCam CCD detector. The scanned Raman shift range is from 100 to 1200 cm^{-1}.

The inductively coupled plasma optical emission spectroscopy (ICP-OES) experiments were conducted on a VARIAN ICP-715ES instrument to verify the element compositions of catalysts.

The scanning electron microscope (SEM) images were taken on a Hitachi SU8010 field emission scanning electron microscope.

The specific surface areas of the catalysts were measured with nitrogen adsorption-desorption at 77 K on an Beijing Beifen ST-08B instrument.

O2-TPD experiments were performed on Micromeritics ASAP 2920 instrument according to the following procedure. Prior to each test, 50 mg sample was first pre-treated in a 30 mL·min^{-1} high purity Ar flow at 400℃ for 30 min to remove any surface impurities. After cooling down to 50 ℃, a 10%O_2/Ar flow with a flow rate of 30 mL·min^{-1} was introduced into the the sample for 60 min to saturate the surface with oxygen. Afterwards, the sample was flushed again with a 30 mL·min^{1} high purity Ar flow for 30 min to remove any physically adsorbed oxygen. O_2-TPD experiment was then performed in the same Ar gas flow by increasing the temperature from 50 to 700 ℃ with a flow rate of 10 ℃·min-1. A thermal conductivity detector (TCD) was used to monitor the signals.

XPS tests were carried out on a PHI-5000C ESCA system using a single Mg-Kα X-ray source operating at 300 W and 15 kV of voltage. The spectra were obtained at ambient temperature with an ultrahigh vacuum. The binding energies were calibrated by using the C 1s peak of graphite at 284.6 eV as a standard.

The EPR spectra were recorded at 77 K (liquid nitrogen) with a JEOL FA-200 EPR spectrometer working in a field 100 kHz and a microwave frequency of 9.06 GHz.

In situ DRIFTS experiments were conducted on a Bruker FTIR spectrometer equipped with an in situ diffuse reflectance pool and an MCT detector cooled by liquid nitrogen. Typically, a spectroscopy was collected in a range of 600–4000 cm^{-1} at 300 ℃ with 132 scans accumulated, and under desired gas atmosphere.

1.3 Activity Test

The catalysts 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, 100 mg catalyst was used for activity evaluation, which resulted in WHSV of 18000 mL·g^{-1}·h^{-1}. A K-type thermocouple was placed on top of the catalyst bed with its head point touching the catalyst bed to monitor the accurate reaction temperatures. To measure the light-off behaviors of the catalysts, all data were collected by increasing the reaction 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, a reaction at each temperature over the catalysts was stabilized at least 30 min to get steady state reaction data.

2. Supplementary results

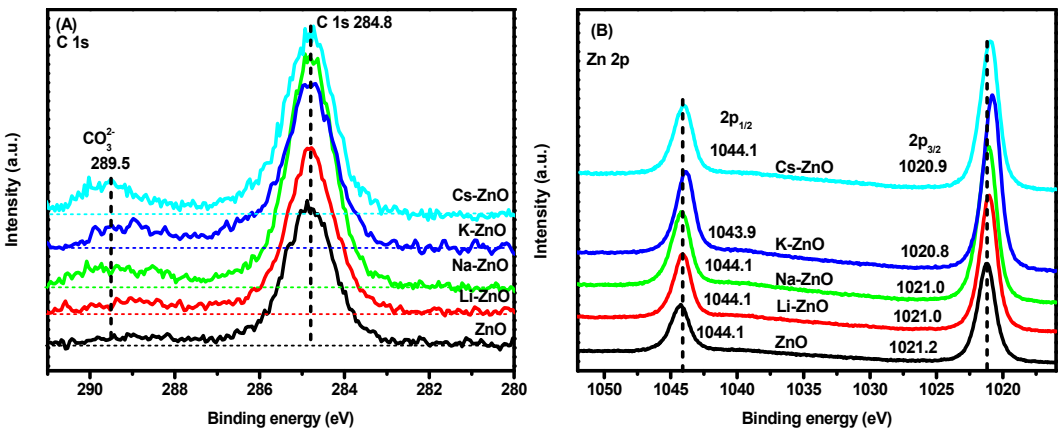

Figure S1 XPS C 1s and Zn 2p spectra of the catalysts.

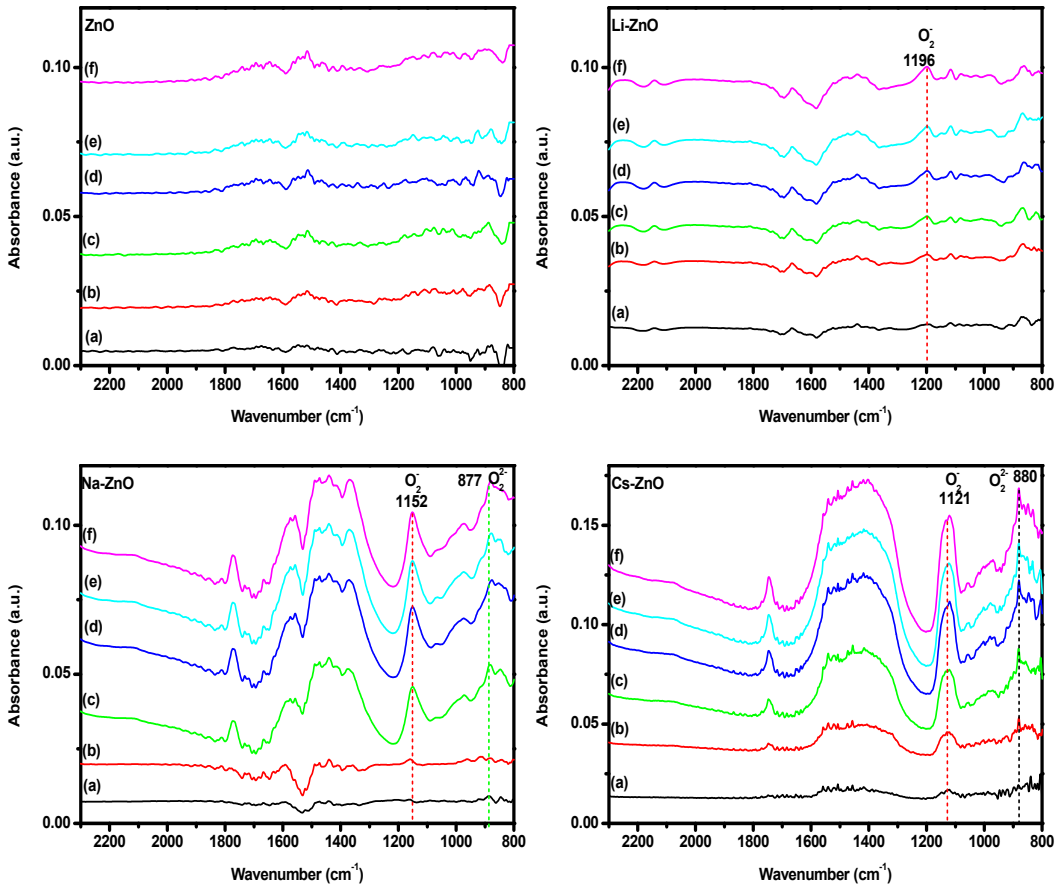

Figure S2. *In situ* DRIFTS study on the reactivity of the surface oxygen species over pure ZnO and Li, Na and Cs modified catalysts at 300℃: (a) 1 min; (b) 3 min; (c) 5 min; (d) 8 min; (e) 11 min; (f) 15 min.

Table S1. Surface element compositions of the catalysts.

Catalysts	Surface elements atomic ratio (%)			
	Zn	O	Alkali metal	C
ZnO	33.34	35.04	-	31.62
Li-ZnO	29.65	30.37	10.75	29.23
Na-ZnO	27.54	32.63	9.04	30.79
K-ZnO	26.86	37.47	10.51	25.16
Cs-ZnO	26.98	38.21	9.82	24.99

References

(1) Julien, C.; El-Farh, L.; Rangan, S.;Massot, S., Studies of LiNi0.6Co0.4O2 cathode

material prepared by the citric acid-assisted sol-gel method for lithium batteries. J. Sol-Gel Sci. Technol. 1999, 15, 63-72.