

Design strategies of surface basicity for NO oxidation over novel Sn-Co-O catalyst in the presence of H₂O

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Electronic Supplementary Information

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1. Catalyst characterization

In this study, the powder X-ray diffraction (XRD) patterns were characterized on a Rigaku D/max-2500 diffractometer. The H₂-TPR was characterized by a Micromeritics ChemiSorb 2720 device. The sample (~50mg) was preheated in a N₂ flow at 350°C for 60min, then it was heated in a 10 % H₂/He flow to make the temperature increased linearly from 50 to 1000 °C at a heating rate of 10 Cmin⁻¹. The depleted amount of H₂ was evaluated by the signal of a thermal conductivity detector. NO+O₂-TPD (temperature-programmed desorption) experiment consisted of three steps: (1) sweep of the sample in N₂ at 350 °C for 1 h; (2) adsorption of NO for about 1 h by passing a gas mixture containing 500 ppm NO + 5% O₂ with N₂ as balance gas and the total flow rate was 200 ml/min through the reactor at 100 °C; (3) TPD measurements were carried out up to 600 °C at a heating rate of 10 °C /min with the total flow rate of 200 ml/min N₂. The in-situ DRIFTS experiments were conducted on a Nicolet 6700 FTIR spectrophotometer and a liquid nitrogen-cooled MCT detector. Prior to each experiment, the sample was pretreated in N₂ flow at 400 °C for 1 h to remove the impurities. After decreasing temperature to 30 °C, the samples were exposed to a NO + O₂ steam for 30 min and a N₂ flow for 10 min to remove the weakly adsorbed NO_x, then the spectra were collected after heating to each desired temperature.

2. CO₂-TPD

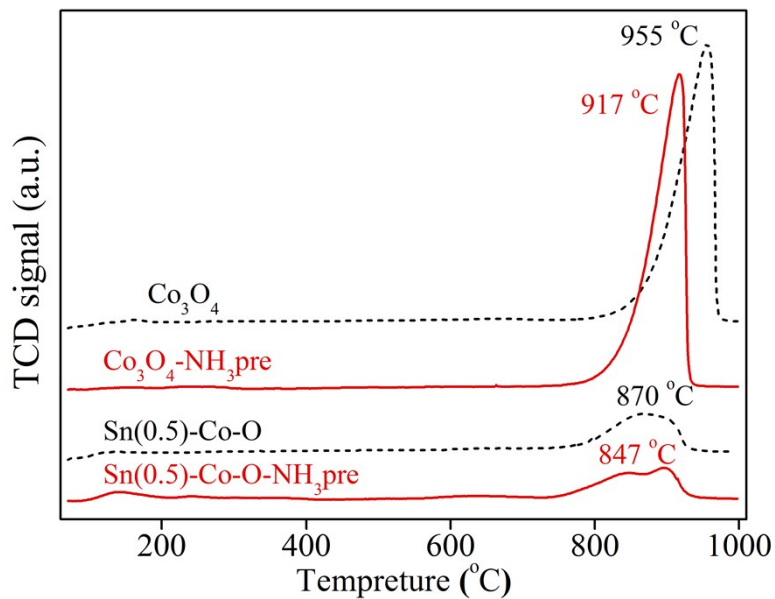


Fig. S1. CO₂-TPD spectra of Sn(0.5)-Co-O and Co₃O₄ catalysts prepared by different precipitants.

3. NO oxidation performance

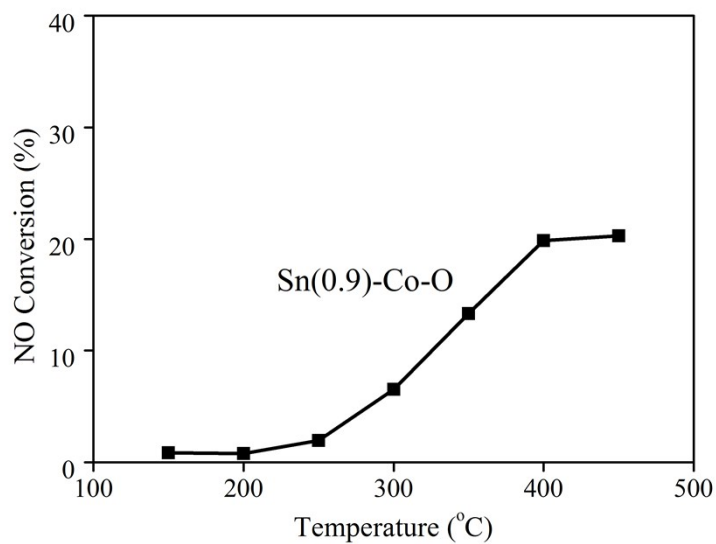


Fig.S2 NO conversion over Sn(0.9)-Co-O catalyst. Reaction conditions: 0.15 g samples, 500 ppm NO, 10 % O₂, N₂ balance, GHSV=3.5×10⁴ h⁻¹.

The Co₃O₄ catalyst showed good NO oxidation activity in a wide temperature range of 250-

300 °C and the best performance was obtained at 300 °C. After addition of Sn, the NO oxidation efficiency was not affected obviously comparing with Co_3O_4 , until the ratio of Sn/(Sn+Co) reached to 0.5. Nevertheless. Meanwhile, the SnO_2 catalyst exhibited nearly no activity in NO oxidation. As reported in literature, the NO oxidation reaction becomes thermodynamic controlled at high temperatures^{1,2}. The activity decreased as the temperature increasing over all of catalyts at >300 °C.

4. XRD analysis

The crystal structure of Sn-Co-O mixed metal oxides catalyts was determined by XRD and the diffraction patterns are shown in Figure S2. For Co_3O_4 catalyst, it could be observed that sharp diffraction peaks appeared which could be attributed to Co_3O_4 . For Sn(0.25)-Co-O and Sn(0.5)-Co-O catalyts, besides the peaks attributed to Co_3O_4 , new peaks correspond to rutile SnO_2 of a tetragonal structure were presented. It indicated that two different crystal structure were formed in these binary metal oxides catalyts.

5. Redox ability

The H_2 -TPR spectra of SnO_2 , Sn-Co-O and Co_3O_4 catalyts are shown in Fig. S2. The Co_3O_4 catalyst displayed two reduction peaks at 320°C and 400°C. According to the results of XRD diffraction, only Co_3O_4 exists in Co_3O_4 catalyst. Therefore, the reduction peak at 320°C can be attributed to the reduction of the catalyst Co_2O_3 to CoO and reduction peak at 400°C could be assigned to CoO to cobalt in Co_3O_4 . This is consistent with the two-step reduction process reported in the literature³. Pure SnO_2 catalyst displayed a overlapping reduction peaks at 480 ~

760 °C, the peak may be attributed to the reduction of SnO₂ to SnO, then to tin^{4,5}.

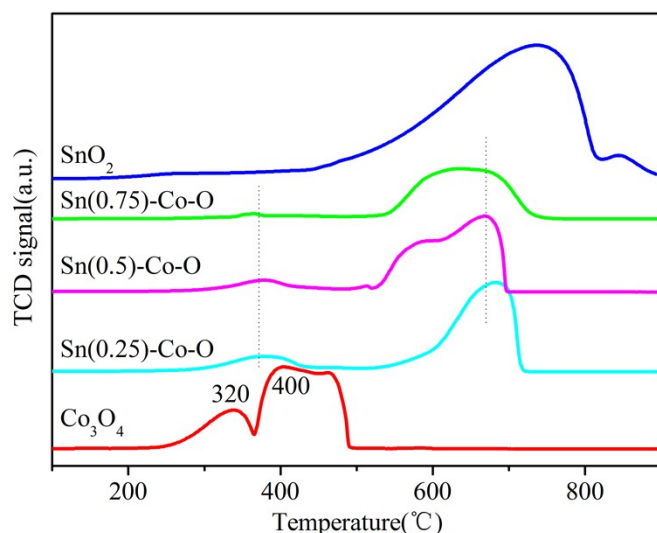


Fig. S3. H₂-TPR spectra of SnO₂, Sn-Co-O , and Co₃O₄ catalysts.

With regard to Sn-Co-O catalysts, there were two overlapping reduction peaks in low temperature range (300°C-400°C) and high temperature range (500°C-700°C) respectively. The low temperature range peak can be attributed to the reduction of Co₃O₄ and the peak at high temperature range reduction could be ascribed to the reduction of SnO_x. Compared with pure Co₃O₄ catalyst, the reduction peak of Sn-Co-O at low-temperature range shift to high temperature and became weaker with increasing Sn content, indicating that doping of Sn affected the redox property of Co₃O₄⁶. Comparatively, the peak attributing to reduction of SnO₂ shifted to lower temperature on Sn-Co-O catalyst than that on SnO₂, indicating the redox property was enhanced on these sample. On the other hand, superior NO oxidation activity was obtained over the Sn(0.75)-Co-O catalyst, indicating that excellent redox property might be not essential in NO oxidation. The NO adsorption behavior is also important in NO oxidation over Sn-Co-O catalysts.

6. In-situ DRIFTS study

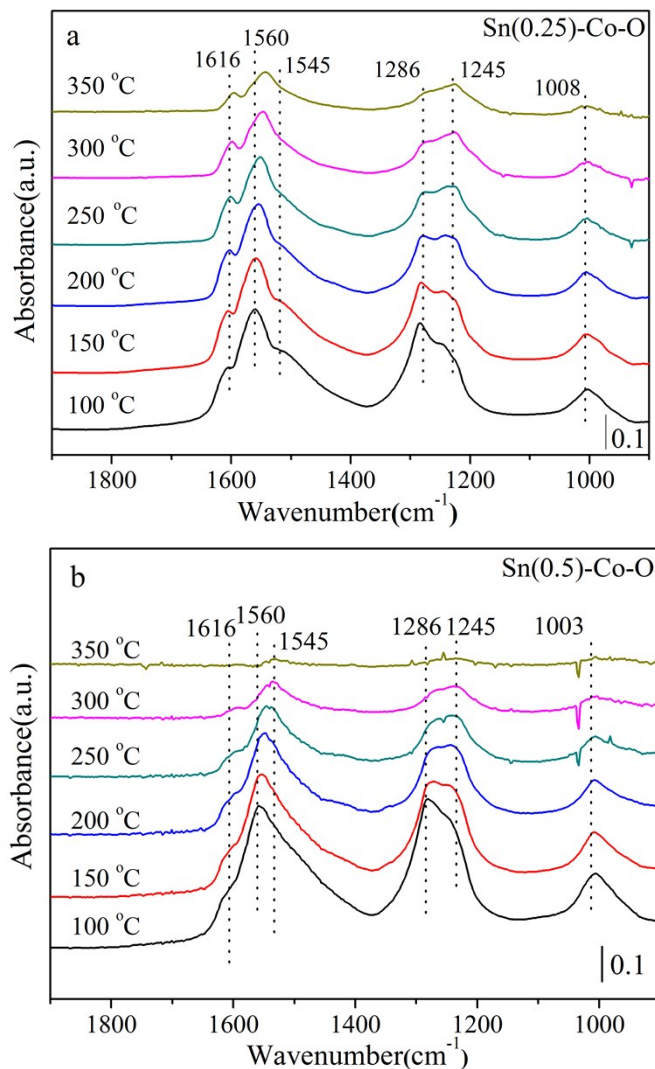


Fig. S4. In-situ DRIFTS spectra of Sn(0.25)-Co-O (a) and Sn(0.5)-Co-O (b) after NO+O₂ adsorption.

According to previous studies, the peaks attributed to bridged bidentate nitrates (at 1616 cm⁻¹), monodentate nitrates (at 1560 cm⁻¹ and 1545 cm⁻¹), bridging nitrates (at 1003-1008 cm⁻¹), and nitrite species (at 1286 cm⁻¹) could be found over two catalysts.⁷⁻⁹ The peaks appeared at 1245-1270 cm⁻¹ could be attributed to nitrites/ HONO species.^{10, 11} Raising the temperature from 100 to 350 °C, the intensity of nitrites decreased rapidly, while nitrates species decreased

continuously and was totally eliminated at 350 °C over Sn(0.5)-Co-O catalyst.

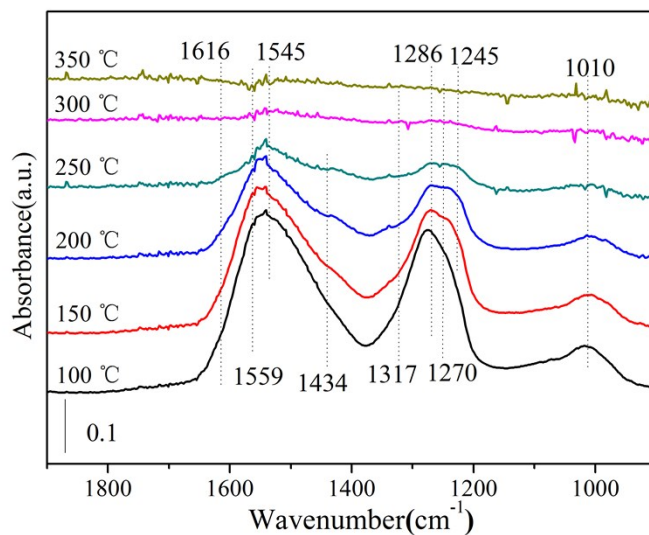


Fig. S5. In-situ DRIFTS spectra of Sn(0.75)-Co-O after NO adsorption.

7. NO oxidation stability test

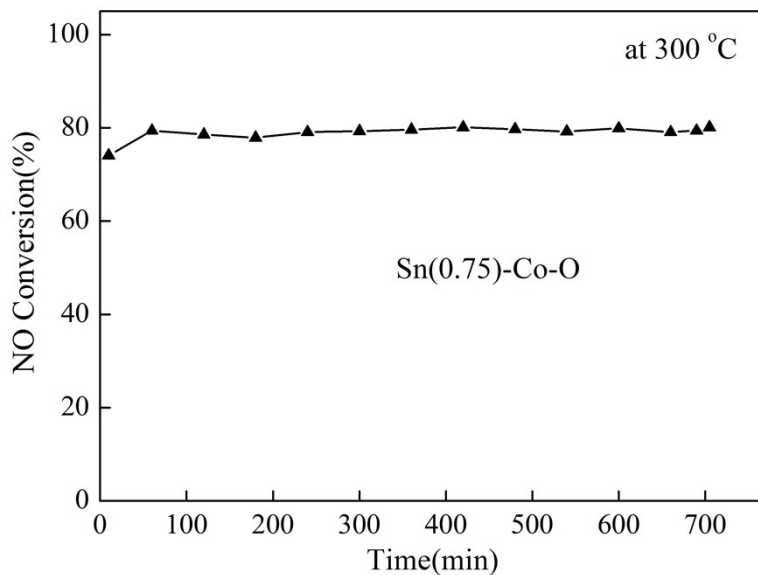


Fig. S6 Stability test of NO oxidation performance over Sn(0.75)-Co-O catalyst.

The NO oxidation stability test with a period of 720 min over Sn(0.75)-Co-O was performed

and the results are shown in Fig. S6. It could be seen the catalytic activity was stable within the test period.

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