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

Huazhen Chang*a, Mingguan Liab,c, Zhenguo Lib, Lei Duana, Chaocheng Zhao*c, Junhua Lib*, and Jiming Haob

a School of Environment and Natural Resources, Renmin University of China, Beijing 100872, China

b State Key Joint Laboratory of Environment Simulation and Pollution Control (SKLESPC), School of Environment, Tsinghua University, Beijing 100084, China

c College of Chemical Engineering, China University of Petroleum, Qingdao 266580, China

Electronic Supplementary Information

* Corresponding author. Tel.: +86-10-62512572; +86-532-86981719; +86-10-62771093;
E-mail address: chz@ruc.edu.cn (H. Chang); zhaochch@upc.edu.cn(C. Zhao); lijunhua@tsinghua.edu.cn (J. Li).
1. Catalyst characterization

In this study, the powder X-ray diffraction (XRD) patterns were characterized on a Rigaku D/max-2500 diffractometer. The H$_2$-TPR was characterized by a Micromeritics ChemiSorb 2720 device. The sample (~50mg) was preheated in a N$_2$ flow at 350°C for 60min, then it was heated in a 10 % H$_2$/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 H$_2$ was evaluated by the signal of a thermal conductivity detector. NO+O$_2$-TPD (temperature-programmed desorption) experiment consisted of three steps: (1) sweep of the sample in N$_2$ at 350 °C for 1 h; (2) adsorption of NO for about 1 h by passing a gas mixture containing 500 ppm NO + 5% O$_2$ with N$_2$ 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 N$_2$. 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 N$_2$ flow at 400 °C for 1 h to remove the impurities. After decreasing temperature to 30 °C, the samples were exposed to a NO + O$_2$ steam for 30 min and a N$_2$ flow for 10 min to remove the weakly adsorbed NO$_x$, then the spectra were collected after heating to each desired temperature.

2. CO$_2$-TPD
Fig. S1. CO$_2$-TPD spectra of Sn(0.5)-Co-O and Co$_3$O$_4$ 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 % O$_2$, N$_2$ balance, GHSV=3.5×10$^4$ h$^{-1}$.

The Co$_3$O$_4$ 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$_3$O$_4$, until the ratio of Sn/(Sn+Co) reached to 0.5. Nevertheless, 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 catalysts was determined by XRD and the diffraction patterns are shown in Figure S2. For Co$_3$O$_4$ catalyst, it could be observed that sharp diffraction peaks appeared which could be attributed to Co$_3$O$_4$. For Sn(0.25)-Co-O and Sn(0.5)-Co-O catalysts, besides the peaks attributed to Co$_3$O$_4$, 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 catalysts.

5. Redox ability

The H$_2$-TPR spectra of SnO$_2$, Sn-Co-O and Co$_3$O$_4$ catalysts are shown in Fig. S2. The Co$_3$O$_4$ catalyst displayed two reduction peaks at 320°C and 400°C. According to the results of XRD diffraction, only Co$_3$O$_4$ exists in Co$_3$O$_4$ catalyst. Therefore, the reduction peak at 320°C can be attributed to the reduction of the catalyst Co$_2$O$_3$ to CoO and reduction peak at 400°C could be assigned to CoO to cobalt in Co$_3$O$_4$. This is consistent with the two-step reduction process reported in the literature $^3$. Pure SnO$_2$ catalyst displayed a overlapping reduction peaks at 480 ~
760 °C, the peak may be attributed to the reduction of SnO$_2$ to SnO, then to tin$^{4,5}$.

![Fig. S3. H$_2$-TPR spectra of SnO$_2$, Sn-Co-O, and Co$_3$O$_4$ catalysts.](image)

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 Co$_3$O$_4$ and the peak at high temperature range reduction could be ascribed to the reduction of SnO$_2$. Compared with pure Co$_3$O$_4$ 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 Co$_3$O$_4$ $^6$. Comparatively, the peak attributing to reduction of SnO$_2$ shifted to lower temperature on Sn-Co-O catalyst than that on SnO$_2$, 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

![In-situ DRIFTS spectra of Sn(0.25)-Co-O (a) and Sn(0.5)-Co-O (b) after NO+O\textsubscript{2} adsorption.](image)

According to previous studies, the peaks attributed to bridged bidentate nitrates (at 1616 cm\textsuperscript{-1}), monodentate nitrates (at 1560 cm\textsuperscript{-1} and 1545 cm\textsuperscript{-1}), bridging nitrates (at 1003-1008 cm\textsuperscript{-1}), and nitrite species (at 1286 cm\textsuperscript{-1}) could be found over two catalysts.\textsuperscript{7-9} The peaks appeared at 1245-1270 cm\textsuperscript{-1} could be attributed to nitrites/ HONO species.\textsuperscript{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.](image)

7. NO oxidation stability test

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

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.

REFERENCES