Supporting Information

# Formation of Highly Active Superoxide Sites on CuO Nanoclusters Encapsulated in SAPO-34 for Catalytic Selective Ammonia Oxidation

Fei Han,<sup>a,‡</sup> Mengqi Yuan,<sup>a,‡</sup> Mine Shinya,<sup>b</sup> Han Sun,<sup>a</sup> Haijun Chen,<sup>\*,a</sup> Takashi Toyao,<sup>c,d</sup> Masaya Matsuoka,<sup>b</sup> Kake Zhu,<sup>e</sup> Jinlong Zhang,<sup>e</sup> Weichao Wang,<sup>a</sup> and Tao Xue.<sup>f</sup>

Email: chenhj@nankai.edu.cn

a Department of Electronics and Tianjin Key Laboratory of Photo-Electronic Thin Film Device and Technology, Nankai University, Tianjin 300 071, PR China.

b Department of Applied Chemistry, Osaka Prefecture University, Gakuen-Cho 1-1, Sakai, Osaka, 599-8531, Japan

c Institute for Catalysis, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan

d Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Katsura, Kyoto 615-8520, Japan

e Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai 200 237, PR China.

f Analysis and Measurement Center, Tianjin University, Tianjin 300 072, China.

### **Catalysts characterization**

 $N_2$  adsorption/desorption experiments were performed at -196 °C on 3H-2000PM2 (BEISHIDE). Prior to analysis, the samples were outgassed under vacuum at 200 °C for 5 h. The specific area of sample was calculated using the Brunauer-Emmett-Teller (BET) equation. The micropore and external surface area and micropore volume were evaluated using t-plot method. X-ray diffraction (XRD) patterns of catalysts were recorded on a Rigaku MiniFlex600 Benchtop X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) at 3-55° and with a scan rate of 2 $\theta = 8.0$  °/min. The composition of catalyst was analyzed by microwave plasma atomic emission spectrometer (MP-AES, Aglient Technology 4210).

Transmission electron microscopy (TEM) images, high angle annular dark field (HAADF) images, and energy dispersive X-ray spectra (EDS) mappings were taken using a FEI Talos F200X S/TEM with a field-emission gun at 200 kV. Electron probe micro-analyzer (EPMA) experiments were carried out on a Shimadzu EPMA 8050 G, the samples were embedded in resin and sliced for detecting elemental distribution on section of samples.

XAFS (XANES and EXAFS) spectra were recorded in the quick scan mode at the BL14B2 facility of SPring-8 at the Japan Synchrotron Radiation Research Institute (JASRI; 8 GeV, 100 mA). The Cu K-edge XAFS spectra were measured in the transmission mode, with a Si (111) double-crystal monochromator at room temperature. The energies were calibrated according to the absorption edge of pure Cu foil. All samples were compressed into pellet. The data reduction and analysis of the XAFS spectra were conducted using the Demeter software package (ATHENA and ARTEMIS, respectively)<sup>1</sup>. The edge step of each spectrum was normalized by subtracting the pre-edge with a linear function and the post-edge with a quadratic function. The energy shift was calibrated by choosing the zero crossing of the second derivative of the

reference spectrum (Cu foil) as E<sub>0</sub> and assigning it to the corresponding tabulated value provided by ATHENA. EXAFS spectra were obtained by subtracting the corresponding XAFS spectra with a background algorithm (AUTOBKG) provided by ATHENA, with  $R_{bkg}$ =1. The k<sup>3</sup>-weighted EXAFS oscillation was Fourier transformed into R space, with the Fourier transformation range between 3.0 and 15 Å<sup>-1</sup>. Curve-fitting analysis was performed on ARTEMIS using input parameters of theoretic models from CIF files of CuO, which has a tenorite structure, by calculation using the FEFF Ver.6L program. The amplitude reduction factors (S<sub>0</sub><sup>2</sup>) and Debye Waller factor ( $\sigma^2$ ) were determined to be 0.836 and 0.0063, respectively, by fitting the experimental data of CuO and fixing the Cu-O coordination number (CN) to be 4. And then, defined S<sub>0</sub><sup>2</sup>=0.836 and  $\sigma^2$ =0.0063, further analysis of the measured samples was performed by using ARTHEMIS. The local structural environments including CN and Radial distance (R) around the absorbing atoms were allowed to vary during the fitting process. The fitted ranges for k and R spaces (k<sup>3</sup>-weighted) were k=3.0-14.0 Å<sup>-1</sup> and R = 1.0-1.8 Å.

In-situ Raman experiments were conducted on RENISHAW Raman spectrometer with an in-situ reaction cell capable of heating and gas purge. The output power was 90 mW, the excitation wave number was fixed, 532 nm, and 50% of output power was employed. The laser was focused on a sample using 50x objective lens, yielding a laser spot size with a diameter of about 1  $\mu$  m. The scattered light was collected by the objective lens and dispersed onto a 2400 grooves/mm grating prior to detection. The powder samples were loaded into an in situ cell equipped with gas inlet and outlet. At the top of cell, it was sealed by a quartz window, which the laser could pass through. The required gas was purged into the cell through gas inlet. The flow rate of gas was controlled with rotameter. The spectroscopy was overlapped for 10 times. The samples were firstly dehydrated in 50 ml/min synthetic air at 400 °C for 1 h. For the sample

activated in nitrogen solely, the activation was conducted in the in-situ cell. Then, after cooled to 30 °C the spectra were collected. As to the in-situ CO Raman experiments, the samples were cooled to 200 °C after the dehydration treatment,  $CO/N_2$  (5000 ppm CO) was purged in for 100 s, then synthetic air was purged in for another 100s. The Raman spectra were recorded every 10 s. The in-situ NH<sub>3</sub> Raman experiments were carried out with the procedure similar as the in-situ CO Raman experiments, while  $CO/N_2$  (5000 ppm CO) was replaced by NH<sub>3</sub>/N<sub>2</sub> (5000 ppm NH<sub>3</sub>).

Temperature-programmed reduction with CO (CO-TPR) and temperature-programmed desorption of  $O_2$  ( $O_2$ -TPD) were performed on a chemisorption analyzer (PCA-1200 Builder Technology). The samples of ca. 120 mg were pre-treated in the flow of synthetic air at 400 °C for 1 h, afterwards cooled to 25 °C in synthetic air for both CO-TPR and  $O_2$ -TPD measurements. For CO-TPR test, the samples were heated at a ramping rate of 5 °C/min from 25 to 700 °C under a flow of 1% CO/He (20 ml/min). The generation of CO<sub>2</sub> was monitored by an online mass spectroscopy detector (ASPEC). O<sub>2</sub>-TPD was carried out in flowing He in the temperature range of 25 to 900 °C. The spectra of CO-TPR and O<sub>2</sub>-TPD were fitted, and the peak areas were normalized by actually mass of samples. The procedures of temperature-programmed surface reaction (TPSR) experiments were similar as CO-TPR and O<sub>2</sub>-TPD. After pre-treated in air, the samples were saturated by 1% NH<sub>3</sub>/He (50 mL/min) at 25 °C. Afterwards, the He (50 mL/min) was purged in for 30 mins to remove the physical absorbed NH<sub>3</sub>. Then the gas was switched to 5% O<sub>2</sub>/He (20 mL/min) and the samples were heated at a ramping rate of 5 °C/min from 25 to 700 °C.

NO-DRIFTS were carried out on a Thermal Scientific Nicolet iS 10 equipped with a MCT detector at a resolution of 4 cm<sup>-1</sup>. ZnSe windows were used in the diffuse reflectance chamber.

Samples were pre-treated under certain conditions, then cooled to 30 °C. The background spectra were collected before the adsorption. After the samples were exposed to NO/N<sub>2</sub> (1% NO) for 30 mins, the spectra were collected. In-situ FT-IR experiments were performed on a Thermal Scientific Nicolet iS 10 equipped with a MCT detector at a resolution of 4 cm<sup>-1</sup>. ZnSe windows were used in the transmission cell. Samples were pre-treated under certain conditions, then cooled to 50 °C. The background spectra were collected before the adsorption. After NH<sub>3</sub> was purged in cell for 30 mins, the gas was shifted to air (20% oxygen and 80% nitrogen) or nitrogen. The spectra were collected at a certain temperature.

#### **Catalysts assessments**

Selective oxidation of ammonia

The catalytic activities of the samples were tested on a fixed bed reactor. 1 ml of catalyst (18-30 mesh) was loaded in quartz tube with a thermocouple inserted into the samples to detect the bed temperature of catalysts. The total gas flow through the catalysts was 1666 ml min<sup>-1</sup>, including 500 ppm NH<sub>3</sub>, 21% O<sub>2</sub>, with N<sub>2</sub> as balance gas, with a GHSV of 100, 000 h<sup>-1</sup>. The temperature was increased from 150 to 400 °C. The composition of gaseous products was monitored by a Thermo Scientific Nicolet iS 10 equipped with a 5M gas cell (PiKE TECHNOLOGIES). Ammonia conversion and N<sub>2</sub> yield at various temperature were calculated by following equation:

$$NH_{3} \text{ conversion } [\%] = \frac{NH_{3 \text{ inlet}} - NH_{3 \text{ outlet}}}{NH_{3 \text{ inlet}}} \times 100[\%] \quad (1)$$

$$N_{2} \text{ yield } [\%] = \frac{NH_{3 \text{ inlet}} - NH_{3 \text{ outlet}} - NO_{2 \text{ outlet}} - 2 \times N_{2}O_{\text{outlet}}}{NH_{3 \text{ inlet}}} \times 100[\%] \quad (2)$$

Kinetic experiments

Before kinetic tests, gas hourly space velocity (GHSV) and particle size of catalysts were optimized to exclude the limitations of internal and external diffusions. As shown in Fig. S15 the reaction rate was nearly constant with different particle size of Cu-TH-6%-N-400. Internal

diffusion limitation was excluded with the particle size was 0.6-0.18 mm. The optimized GHSV was 250, 000 h<sup>-1</sup>. At this GHSV the external diffusion limitation was excluded in the temperature range of 150-225 °C.

During the measurement of activation energy, the GHSV and particle size were 250, 000  $h^{-1}$  and 0.18-0.3 mm, respectively. The conversion of NH<sub>3</sub> was less than 20%. The turnover frequency (TOF) value defined as the number of NH<sub>3</sub> molecule converted per minute per gram in sample, was calculated by the following equation:

Reaction Rate = 
$$\frac{X_{NH_3}[\%] \times F_{NH_3}[mL \cdot min^{-1}] \times C_{NH_3}[ppm]}{m_{catal}[g] \times 22.4[L \cdot mol^{-1}] \times 1,000,000 \times 1000[mL \cdot L^{-1}]} \times 100[\%]$$

The apparent activation energy was calculated from the Arrhenius plots.

The correlation between relative content of Cu (II) superoxo species and reaction rates was calculate. The reaction rates were calculated as  $[R_x(reaction rate)] = [R_x(N_2)] - [R_x(A)]$  and relative content of Cu (II) superoxo species were calculated as  $[N_x(superoxo)] = [S_x(N_2)] - [S_x(A)]$ .

## **Computational methods**

The structural optimizations and infrared vibration spectra have been carried out using the projector-augmented wave (PAW) approach within Vienna ab initio simulation package (VASP).<sup>2</sup> General Gradient Approximation (GGA) with Perdew-Burke-Ernzehof (PBE) functional was employed to describe the exchange-correlation potential. The plane-wave cut off energy of 520 eV was adopted and Monkhorst-Pack k-point grids of  $3\times3\times1$  were set up in all calculations. The structural optimization stopped when the force of each atom was less than 0.05 eV/Å, and the convergence criteria of total energy was set to be 10-4 eV. CuO (111) surface was constructed by using a (2×2) supercell. A vacuum layer of 15Å was added to construct the slab

supercell models and the bottom layer is well passivated by H atoms. Two atomic layers at the bottom were fixed whereas the other four surface atomic layers were fully relaxed. As shown in Fig. S17 the infrared vibration of NH<sub>3</sub> adsorbed on Cu (II) superoxo was also simulated on the CuO (111) surface. The bond length of Cu-N and O-O of Cu (II) superoxo was referred according to the published data<sup>3-6</sup>. The bond length of Cu-O of Cu (II) superoxo was adopted according to XAFS results.

Samples	BET	T-Plot	BJH	Loading of Cu (%)
	(m²/g)	$(m^{2}/g)$	(ml/g)	
Cu@SAPO-34	474	422	0.0701	3.3
Cu-IWI-3%-N-400	684	632.1	0.0653	1.6
Cu-IWI-6%-N-400	663	622.1	0.0540	4.4
Cu/Y-N-400	n.a	n.a	n.a	9.4
Cu-TH-6%-A	480	438	0.0917	5.4
Cu-TH-6%-N	460	414	0.0853	
Cu-TH-6%-N-150	466	420	0.0891	
Cu-TH-6%-N -400	463	422	0.0804	

**Table S1.** Texture properties of samples. The loading of Cu in catalysts was determined by

 microwave plasma atomic emission spectra (MP-AES).

The total areas, microporous areas, and volume of pores were calculated by BET, T-plot, and BJH method, respectively. The samples prepared by Trojan Horse approach shared the similar textural properties with the sample of Cu@SAPO-34. The samples prepared by incipient wetness impregnation method showed total areas and microporous areas higher than the samples prepared by Trojan Horse approach.



**Figure S1.** HAADF images of a) Cu-TH-6%, EDS mapping of elements b) Cu, c) Al, d) Si, e) P, f) O.



**Figure S2.** XRD patterns of samples. The specific peaks of CuO in sample labeled as (g) were highlighted in red circle.

All samples showed obvious characteristic peaks of CHA type zeolite. The intensities of peaks were same indicating the structure of SAPO-34 was maintained in all samples. The absence of specific peaks of CuO in the Cu-TH samples indicates the highly dispersion of CuO nanoclusters present in SAPO-34. The peaks due to CuO particles emerged in the samples prepared by incipient wetness impregnation method with the high loading of Cu.



Figure S3. TEM results of a) Cu-IWI-3%-N-400; b) Cu-IWI-6%-N-400; c) Cu-TH-6%-A; d) HR-TEM results of Cu-TH-6%-A.

As shown in Fig. S2a, no obvious CuO nano-particles were detected in the sample of Cu-IWI-3%-N-400, indicating Cu species are highly dispersed in the sample with low loading of copper. CuO particles with the size of more than 10 nm were detected for Cu-IWI-6%-N-400 (Fig. S2b). Fig. S2c show TEM results of Cu-TH-6%-A prepared by Trojan Horse approach. Well dispersion of CuO clusters (3-4 nm) was demonstrated. The interplanar spacing is 0.229 nm corresponding to (111) crystal plane of CuO.



Figure S4. EDS mapping of Al, Si, P, and O elements in the sample of Cu@SAPO-34.



Figure S5. EDS mapping of Al, Si, P, and O elements in the sample of Cu-TH-6%-A.



Figure S6. EDS mapping of Al, Si, P, and O elements in the sample of Cu-TH-6%-N-400.



Figure S7. EDS mapping of Al, Si, P, and O elements in the sample of Cu-IWI-6%-N-400.



Figure S8. EPMA images a) Cu@SAPO-34-A; c) Cu@SAPO-34-N-400; e) Cu-TH-6%-A; g) Cu-TH-6%-N-400 and Cu mappings of: b) Cu@SAPO-34-A; d) Cu@SAPO-34-N-400; f) Cu-TH-6%-A; h) Cu-TH-6%-N-400.



Figure S9. Selectivity of NH<sub>3</sub>-SCO reactions of the samples prepared by Trojan Horse approach.



**Figure S10.** Catalytic performance of the samples prepared by Trojan Horse approach activated at different conditions. The loading of copper is same as Cu-TH- 6%. The samples are denoted as (N or A)-T-t, where N or A refers to the activation in nitrogen or air, respectively. T refers to the activation temperature (°C), and t refers to activation time (h).



Figure S11. Raman spectrum of H-SAPO-34 zeolite.



Figure S12. Raman spectra of Cu@SAPO-34-N-400 and Cu@SAPO-34.

Raman spectra of Cu@SAPO-34-N-400 and Cu@SAPO-34 showed no specific peaks of Cu

(II) superoxo species.



Figure S13. CO-TPR results of Cu@SAPO-34 and Cu-TH-6%.

Cu@SAPO-34 only shows a very weak peak at around 217 °C after the nitrogen activation and successive re-oxidation at 400 °C. It is noteworthy that Cu-TH-6%-N-400 shows an obvious reduction peak at 217 °C comparing with Cu-TH-6%-A. Considering almost no Cu (II) superoxo species present in the samples of Cu@SAPO-34-N-400, Cu@SAPO-34-A, as evidenced by Raman spectra, the peak at 217 °C can be ascribed to the reduction of Cu (II) superoxo species.



Figure S14. O<sub>2</sub>-TPD results of Cu-TH-6%-N-400 and Cu-IWI-6%-N-400.



**Figure S15.** The deconvolution of O<sub>2</sub>-TPD: a) Cu@SAPO-34-N-400; b) Cu-TH-4%-N-400; c) Cu-TH-5%-N-400; d) Cu-TH-6%-N-400.

The areas of peaks located from 300-600 °C were calculated and denoted as S-x (N<sub>2</sub> or A) where x, N<sub>2</sub>, and A refer to content of copper, activated in N<sub>2</sub>, and activated in air, respectively. The relative content of Cu (II) superoxo species was calculated as [N (superoxo)] = [S-x (N<sub>2</sub>)] – [S-x (A)].



**Figure S16.** The possibility of internal and external diffusion limitation was assessed by series experiments at different temperature with varied a) particles size and b) GHSV, respectively. (I) 150 °C; (II) 175 °C; (III) 200 °C; (IV) 225 °C; (V) 250 °C; (VI) 275 °C; (VII) 300 °C.

The reaction rate was nearly constant with different particle size of Cu-TH-6%-N-400. Internal diffusion limitation was excluded with the particle size was 0.6-0.18 mm. The optimized GHSV was 250, 000 h<sup>-1</sup>. At this GHSV the external diffusion limitation was excluded in the temperature range of 150-225 °C.



**Figure S17.** The adsorption of NH<sub>3</sub> on Cu (II) superoxo at the CuO (111) surface. The pink, red, blue, and light gray balls represent Cu, O, N, and H atoms, respectively.

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