Controlling dynamic structural transformation of atomically dispersed CuO_x species and influences on their catalytic performances

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ABSTRACT

Understanding the dynamic structural transformation of subnanometric metal species is a key to the establishment of the structure-reactivity relationship for heterogeneous catalysts composed of single atoms and subnanometric clusters. Unlike noble metal catalysts, the evolution of non-noble metal catalysts containing singly dispersed atoms and clusters during redox treatments and under reaction conditions has not been well understood yet. In this work, with spectroscopic techniques and aberration-corrected electron microscopy, the control of dynamic structural transformations of supported CuO_x species (from single ions to nanoclusters and nanoparticles) by the combination of redox and water treatment have been systematically studied. Furthermore, their catalytic properties for two deNO_x reactions ($\text{NO}+\text{CO}$, $\text{NH}_3+\text{NO}+\text{O}_2$) have also been demonstrated to be strongly related to the dispersion of Cu^{2+} species, providing insights on the active sites in these model reactions for deNO_x applications.

KEYWORDS. Copper oxide, structural transformation, dispersion control, deNO_x, H_2O

INTRODUCTION

Developments of characterization techniques in the last decade have advanced our understanding of the active sites in heterogeneous catalysis.^{1,2} One significant improvement is the recognition of the importance of dynamic transformation of active species during the catalytic process, the influences of the transformation on the catalytic properties, and the control of these transformations.³ By *in situ* spectroscopic and microscopic techniques, the structural dynamic changes (including changes in chemical compositions, nanoscale morphology, and atomic rearrangement) of metal nanoparticles have been revealed.^{4,5} It has been demonstrated that the structure of metal catalysts can transform among single atoms, nanoclusters and nanoparticles depending on the reaction conditions.⁶ Besides, the structural transformation behavior is strongly related to the size of the metal species. The structural evolution of subnanometric metal species, including single atoms and metal clusters with a few atoms, under reaction conditions or during various treatment procedures is more sensitive than the corresponding nanoparticles.

Most of the previous works are focused on the transformation of noble metal catalysts (like Au, Pt, Ru, etc.), of which the dynamic behaviors under reaction conditions have been studied by various *in situ* techniques, like *in situ* X-ray absorption spectroscopy (XAS),⁷ *in situ* transmission electron microscopy (TEM)⁸⁻¹¹ and *in situ* X-ray photoelectron spectroscopy (XPS).^{12,13} Pt, for instance, undergo structural evolution under different conditions. Reconstruction on the surface of large Pt particles has been reported under different atmosphere.^{14,15} For smaller Pt clusters or even single atoms, the dispersion of Pt species can be tuned, it has been revealed that reversible transformation of Pt atoms or clusters confined in the zeolite pores would occur when switching the oxidative/reductive atmosphere.⁷ Similar findings were also reported on supported

Pt catalysts such as Pt/ γ -Al₂O₃. At high temperature, Pt single atoms are stable in O₂, yet these Pt atoms tend to cluster in CO oxidation environment and to be reduced in H₂.^{16, 17} Moreover, agglomerated Pt would redisperse in oxidative environment such as NO and O₂.^{18, 19} These discoveries provide new insights in understanding the activities and stabilities of noble metal catalysts. For non-noble metals and metal oxides, however, there are few works on their dynamic changes during various treatments or under catalytic reaction conditions, and even fewer of their impact on the catalytic properties or the control of these transformations. Due to their distinct physicochemical properties between metallic state and metal oxide state, the dynamic transformations during the catalytic processes will be more complicated than those of noble metal catalysts.²⁰ The complicated structural changes of non-noble metal catalysts under reaction conditions (including the chemical states, particle size, and metal-support interaction) make it more difficult to clarify their effects in the catalytic process.^{21, 22}

Cu-based catalysts have been widely applied for heterogeneous catalysis for energy²³ and environmental²⁴ purposes. The impact of the geometric factor of CuO_x species on the catalytic performances has been extensively studied. For deNO_x reactions such as the NH₃-SCR reaction or the NO+CO reaction, Cu species confined in zeolites²⁴ or supported on the oxide carriers²⁵ have shown superior activities. There are many reports on this subject concerning CuO_x dispersions. For example, isolated Cu atoms in zeolite pores have been found to be the active sites for the NH₃-SCR reaction.²⁶⁻²⁹ For CuO_x species supported on the oxide carriers such as γ -Al₂O₃, there are also studies on the CuO_x dispersions. The control of the dispersion was mainly achieved by varying the loading amount of Cu.³⁰ The dynamic change of Cu species under different conditions, however, has not been systemically studied. Recent works have shown the migration of Cu species in zeolite crystallites under the NH₃-SCR reaction conditions.^{24, 31-34}

However, comparing with Cu species confined in zeolite structures, of which the coordination environment can be well characterized by *in situ* XAS,^{26, 35} it is practically more challenging to identify the evolution of Cu species supported on solid carriers with open surface structures, such as TiO₂, Al₂O₃, and ZrO₂, let alone the observation of the impact on the catalytic behavior or the control of these transformations.³⁶

In this work, by employing CuO supported on γ -Al₂O₃ as model catalysts, we have performed a systematic study on the control of the dynamic structural transformation of CuO species during redox processes. By different types of spectroscopic techniques and aberration-corrected electron microscopy, we have correlated the dynamic structural transformations of CuO species with their sizes and surface concentrations. It is found that a combined moisture and redox treatment can modulate the agglomeration and redispersion of supported Cu species, which governs the redox properties and further influences the catalytic performances of two deNO_x reactions (NO+CO, NH₃-NO+O₂), providing insights on the recognition of active sites in these model reactions for deNO_x applications.

EXPERIMENTAL SECTION

Sample preparation. The γ -Al₂O₃ used in this work was purchased from Fushun Petrochemical Institute in China. It was calcined in flowing air at 650 °C for 6 h before use. Its Brunauer-Emmett-Teller (BET) surface area was 118 m² g⁻¹, determined by N₂ adsorption and desorption isotherms. A series of CuO/ γ -Al₂O₃ samples with different CuO loading were prepared by conventional wet impregnating γ -Al₂O₃ with aqueous solutions containing calculated amount of Cu(NO₃)₂·3H₂O. The catalysts are denoted as xCuAl where x represent for the loading amount of CuO on γ -Al₂O₃. e.g., 04CuAl stands for the sample with CuO loading amount of 0.4 mmol/100 m² γ -Al₂O₃. Take 04CuAl as an example, 2 g of γ -Al₂O₃ powder was dispersed in 50 mL DI H₂O. A 20 mL solution containing 228 mg Cu(NO₃)₂·3H₂O was added to the dispersion dropwise. The mixture was then vigorously stirred for 2 h at room temperature before being evaporated at 100 °C to remove the water. The resulting samples were dried overnight, grinded and then calcined at 550 °C for 5h in air, with a heating ramp of 2 °C/min.

The diluted xCuAl (denoted as D-xCuAl, thereafter) have been prepared by physical dilution of xCuAl with a calculated amount of γ -Al₂O₃. The atomic ratio of CuAl in D-xCuAl samples are kept the same with 01CuAl.

Pretreatment procedure for CuO/ γ -Al₂O₃ catalysts. The sample pretreatments were performed in a micro-reactor or a reaction chamber. The xCuAl samples were exposed in a 30 mL/min Ar-H₂ mixture stream (7.0 % H₂ by volume) at 500 °C for 30 min. They are denoted as xCuAl-H. Then the xCuAl-H samples were treated in a dried O₂-N₂ mixture stream at a rate of 30 mL/min (20 % O₂ by volume, denoted as dry air) at 300 °C for 30 min, the resultant samples are denoted as xCuAl-HO. Besides, the xCuAl-H samples were also treated in moisture containing O₂-N₂ mixture stream at a rate of 30 mL/min (20 % O₂ by volume, denoted as wet air)

at 300 °C for 30 min, the resultant samples are denoted as xCuAl-HW. The moisture contained in the wet air was controlled by passing the dry air (30 mL/min) through a bubbler at 25 °C, corresponding to a partial pressure of ~3 kPa for water calculated according to the Dalton's Law.

Sample characterizations. X-ray diffraction (XRD) patterns were recorded on a Philips X'pert Pro diffractometer using Ni-filtered Cu Ka radiation ($\lambda=0.15418$ nm). The X-ray tube was operated at 40 kV and 40 mA. The relative intensities of the peaks at $2\theta = 35.6^\circ$ and $2\theta = 45.9^\circ$ was chosen to compare the relevant intensities of samples with different loadings.³⁷⁻³⁹

Brunauer–Emmett–Teller (BET) surface areas were measured by nitrogen adsorption at 77 K on a Micrometrics ASAP2020 adsorption apparatus. Before adsorption measurements, the samples were degassed for 3 h at 300 °C.

The *in situ* X-ray photoelectron spectroscopy (*in situ* XPS) analysis was performed on a PHI 5000 VersaProbe system, using monochromatic Al Ka radiation (1486.6 eV). In the case of the pretreated sample, the as-prepared catalysts were placed in the introduction chamber (IC) and then were transferred to the reaction chamber (RC) by a transfer rod. After degassing the RC, the samples were pretreated as described in the above section of sample pretreatment. As the temperature was cooled down to room temperature, RC was degassed again and the samples were transferred back to IC. Subsequently, the samples were transferred to the main chamber (MC) for XPS measurement. The binding energies (± 0.1 eV) were referenced to the Al 2p peak at 74.0 eV.

Electron paramagnetic resonance (EPR) measurements were performed on a Bruker EMX-10/12 X-band spectrometer operating at a frequency of $\nu \approx 9.48$ GHz, and 100 kHz field modulation was used for the measurements. The spectra for all catalysts were recorded at 110 K.

The peak intensity of $g_{\perp} = 2.0$ was chosen to compare the relative intensities of D-xCuAl sample series.

Temperature-programmed reduction (TPR) was carried out in a quartz U-tube reactor using 50 mg sample for each measurement. The sample was pretreated at 300 °C in N₂ stream for 1 h. After that, TPR started from room temperature at a rate of 10 °C min⁻¹ in a mixed H₂-Ar stream (7% H₂ by volume). The effluent gas was continuously analyzed by a thermal conductivity detector.

Aberration-corrected STEM observations were performed with a probe corrected FEI Titan 80-300 electron microscope. The observations were done in Scanning Transmission Electron Microscopy (STEM) mode using a High Angle Annular Dark Field Detector (HAADF). The probe convergence angle was approximately 18 mrad and the inner detection angle on the HAADF detector was approximately 3 times higher than the probe convergence angle. Sample preparation was performed by dispersing the catalytic powder on lacey carbon on a Mo TEM grid. To illustrate the dynamic structure transformation of CuO_x species under different treatments more clearly, the pseudo-colored images of certain areas in the STEM-HAADF images are provided. These were accomplished by Digital Micrograph[®] software, which converts Z-contrast into heat maps. Specifically, brighter spots in the original images were processed into warmer color (red). **Figure S1** shows an example of this operation.

The X-ray absorption fine structure (XAFS) spectra at Cu K ($E_0 = 8979$ eV) edge was performed at BL14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF) operated at 3.5 GeV under “top-up” mode with a constant current of 250 mA.⁴⁰ The XAFS data were recorded under transmission mode with two Oxford ion chambers. The energy was calibrated accordingly to the absorption edge of pure Cu foil. Athena and Artemis codes were used to

extract the data and fit the profiles. For the X-ray absorption near edge structure (XANES) part, the experimental absorption coefficients as a function of energies $\mu(E)$ were processed by background subtraction and normalization procedures, and reported as “normalized absorption” with $E_0 = 8979.0$ eV for all tested samples and Cu foil/CuO/Cu₂O standard. For the extended X-ray absorption fine structure (EXAFS) part, the Fourier transformed (FT) data in R space were analyzed by applying first-shell approximate model for Cu-N contribution. The passive electron factors, S_0^2 , were determined by fitting the experimental data on Cu foil and fixing the coordination number (CN) of Cu-Cu to be 12, and then fixed for further analysis of the measured samples. The parameters describing the electronic properties (e.g., correction to the photoelectron energy origin, E_0) and local structure environment including CN , bond distance (R) and Debye-Waller factor around the absorbing atoms were allowed to vary during the fit process. The fitted ranges for k and R spaces were selected to be $k = 3-12 \text{ \AA}^{-1}$ with $R = 1.0-3.5 \text{ \AA}$ (k^3 weighted).

Catalytic activity tests. The NO reduction by CO model reaction tests were performed in a fixed-bed reactor with 50 mg catalyst. The feed gas contains 2.5 % NO, 5 % CO and 92.5 % He by volume. The total flow rate of the feed gas was 10 mL min^{-1} , corresponding to a space velocity of approximately $12\,000 \text{ h}^{-1}$. A gas chromatography with two columns and two thermal conductivity detectors were used for analyzing the product. Column A with Paropak Q for separating N₂O and CO₂, and column B packed with 5A and 13X molecule sieve (40–60 M) for separating N₂, NO, and CO.

The NO conversion is calculated by

$$\text{NO conversion} = \left(1 - \frac{[\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}}\right) \times 100\%$$

The N₂ selectivity is calculated by

$$\text{N}_2 \text{ selectivity} = \left(\frac{[\text{N}_2]_{\text{out}} \times 2}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}} \right) \times 100\%$$

The NH₃-SCR activity tests were performed in a fixed-bed reactor with 0.2 g catalyst. The feed gas contains 500 ppm NO, 500 ppm NH₃ and 5 vol% O₂ with N₂ as diluents. The total flow rate of the feed gas was 100 mL min⁻¹, corresponding to a space velocity of approximately 30 000 h⁻¹. The effluent gas was continuously analyzed at 150 °C by an online Thermo Fischer IS10 FTIR spectrometer equipped with a 2 m path-length gas cell (250 mL volume).

The NO conversion is calculated by

$$\text{NO conversion} = \left(1 - \frac{[\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \right) \times 100\%$$

The N₂ selectivity is calculated by

$$\text{N}_2 \text{ selectivity} = \left(\frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}} - [\text{NO}_2]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}} \right) \times 100\%$$

RESULTS AND DISCUSSION

Figure 1. (a) XRD patterns of pristine CuAl samples and γ -Al₂O₃; (b) XPS of Cu 2p_{3/2} region of pristine CuAl samples; (c) EPR spectra of 01CuAl and diluted CuAl samples with higher CuO loading; (d) Relative intensity of CuO diffraction peak vs. γ -Al₂O₃ diffraction peak for various CuAl samples, derived from XRD results; (e) Atomic ratio of Cu to Al in various CuAl samples, calculated based on the XPS results; (f) The EPR signal intensities. The signal intensities are evaluated from twice integration of EPR spectra.

Study of the dispersion of CuO_x species on pristine samples. The supported CuO/ γ -Al₂O₃ samples (denoted as xCuAl, x being the loading amount of CuO on γ -Al₂O₃. e.g., 04CuAl for the

sample with CuO loading amount of 0.4 mmol/100 m² γ -Al₂O₃, thereafter) with various loading amount of CuO are prepared by wet impregnation of Cu(NO₃)₂ on γ -Al₂O₃, followed by calcination in air. As can be seen in **Figure 1a**, the diffraction peaks corresponding to crystalline CuO appear when the CuO loading is higher than 0.6CuAl. Their intensities show a linear relationship with CuO loadings (**Figure 1d**), suggesting that the size and the amount of crystalline CuO species increases with the CuO loading. Meanwhile, the XRD patterns are almost identical with pure γ -Al₂O₃ when the CuO loading is lower than 0.6CuAl. Considering the detection limit of XRD, most of the CuO species should exist as very small particles (<3 nm) or even atomically dispersed Cu²⁺ sites in CuAl samples with low CuO loading, which will be further elucidated by STEM studies.

The chemical states of Cu species supported on γ -Al₂O₃ have been studied by XPS. For Cu 2p_{3/2} region, peaks at ~934.0 eV corresponds to Cu²⁺ species, which would be further confirmed by the satellite peak at ~942.5 eV.⁴¹ As shown in **Figure 1b**, according to the binding energy in the XPS spectra, the Cu species supported on γ -Al₂O₃ exist as Cu²⁺ species for all the CuAl samples. Furthermore, the dispersion of Cu species in various CuAl samples has also been evaluated based on the surface atomic ratio of Cu and Al calculated according to the XPS spectra. As can be seen in **Figure 1e**, the Cu/Al ratio increases almost linearly with the loading of CuO in the range of 0.1 to 0.6 mmol/100 m². When the CuO loading exceeds 0.7 mmol/100 m², the Cu/Al ratio does not change much. It is implied by the XRD patterns and Cu/Al ratios derived from XPS spectra that CuO species mainly exist as highly dispersed species or small CuO clusters on γ -Al₂O₃ when the loading is below 0.6 mmol/100 m², and form agglomerated CuO nanoparticles (as observed in XRD patterns) when the loading exceeds 0.7 mmol/100 m².

It has been shown in previous works that the dispersion of CuO species in supported catalysts can be studied by electron paramagnetic resonance (EPR) spectroscopy, especially in Cu/Al₂O₃ system.^{30, 42-45} Therefore, the 01CuAl and the diluted CuAl samples with higher CuO loadings (D-xCuAl) have been studied by EPR. Highly dispersed Cu²⁺ species is EPR active due to the unpaired electron in the d_x²-d_y² orbital of the d⁹ electron configuration. However, the coupling of the magnetic dipole moment of neighboring Cu²⁺ may broaden or even mute the EPR signal as Cu²⁺ ions get closer.⁴⁵ The Cu²⁺-O-Cu²⁺ networks are even EPR inactive, which could indicate the agglomeration of Cu²⁺ caused by increasing the Cu loadings⁴⁵ or the reduction/oxidation procedure. In other words, the EPR intensities of the sample are positively correlative to the amount of isolated Cu²⁺ ions. The further Cu²⁺ ions are apart, the stronger the intensities are. Since the total amounts of CuO species in all the tested samples are kept the same by dilution, the dispersion of CuO species can be indicated from the comparison of the EPR signal intensities of different samples. As can be seen in **Figure 1c and 1f**, the EPR intensity decreases when increasing the CuO loadings in the pristine D-CuAl samples, indicating that Cu²⁺ species get closer or even cluster with the increasing loadings of CuO, which is consistent with the XRD and XPS results.

Figure 2. Aberration-corrected high-resolution STEM images of (a) pristine 01CuAl sample, (b) pristine 04CuAl sample and (c) pristine 10CuAl sample. (d), (e) and (f) are the heat maps of the red squares in (a), (b) and (c), respectively. In these heat maps, Cu ions with higher contrast can be easily distinguished from the γ -Al₂O₃ support. (g), (h) and (i) are the schematic evolution of the size of CuO species supported on γ -Al₂O₃ with the CuO loading. By tuning the CuO loadings, it is feasible to modulate the majority of CuO species on γ -Al₂O₃ support, ranging from atomically dispersed Cu²⁺ species to subnanometric CuO clusters to CuO nanoparticles.

According to the above spectroscopic studies, it is proposed that the dispersion of CuO species is strongly related to the CuO loadings. To directly study the atomic structures of the supported CuO species, CuAl samples with different CuO loadings have been investigated by aberration-corrected high-resolution scanning transmission electron microscopy (AC-HR-STEM). As shown in **Figure 2a**, a large amount of singly dispersed Cu²⁺ sites with very few CuO clusters can be observed on γ -Al₂O₃ support in the pristine 01CuAl sample. When the CuO loading increases to 0.4 mmol/100 m², a considerable number of subnanometric CuO clusters can be observed while the majority of Cu species still remain to be singly dispersed Cu²⁺ sites on the γ -Al₂O₃ support (see **Figure 2b**), which rules out the possibility that the little Cu amount extinguishes the possible XRD signal of any kind of agglomerated Cu species. It should be noted that the location of the singly dispersed Cu²⁺ sites are probably in the octahedral vacancy formed by oxygen atoms (see **Figure S2 and S3**), which is previously predicted by an “incorporation model”.^{37, 46} As observed in both 01CuAl and 04CuAl samples, Cu²⁺ ions appear to be located on the surface vacancy sites formed by oxygen. In other words, the position of Cu atoms supported on the surface is basically similar to the position of Al³⁺ in the solid carrier, which is consistent with the observation in single-atom catalysts based on noble metals (such as Au, Pt, etc).⁴⁷ Further increasing the CuO loading to 1.0 mmol/100 m² leads to the formation of a large number of CuO clusters on γ -Al₂O₃. Nevertheless, a few singly dispersed Cu²⁺ sites can also be observed in the 10CuAl sample (see **Figure 2c**).

Based on the above structural characterizations, it can be concluded that the dispersion of CuO species on γ -Al₂O₃ changes as the loadings of CuO changes, which is illustrated in **Figure 2g-i**. For CuAl samples with CuO loading below 0.2 mmol/100 m², CuO species mainly exist as atomically dispersed Cu²⁺ sites due to its very low CuO loading. For CuAl samples with a

loading of 0.2 to 0.6 mmol/100 m², both atomically dispersed Cu²⁺ sites and CuO clusters with several atoms are present. When the CuO loading is further increased to 0.7 mmol/100 m² or higher, the amount of agglomerated CuO increases and large CuO nanoparticles appear, which can also be determined by the XRD patterns and EPR spectra (see **Figure 1**).

Study the evolution of CuO/ γ -Al₂O₃ samples during redox treatments. the reduction-oxidation treatment has significant influences on the physicochemical properties of catalysts for redox processes, which has already been studied for noble metal catalysts, such as Pt and Pd.^{7, 48} Herein, we introduce the study on the influence of reduction-oxidation treatments on CuO/ γ -Al₂O₃ catalysts. The pristine CuAl samples were reduced by H₂ at 500 °C (denoted as CuAl-H thereafter). Taking into consideration that, water is commonly present in many catalytic processes (such as TWC⁴⁹ and NH₃-SCR processes^{24, 31, 32}), we have also studied the influence of H₂O on the redox properties of CuAl samples. The reduced samples CuAl-H were re-oxidized by dry air (without moisture) or wet air (with moisture), denoted as CuAl-HO or CuAl-HW, respectively.

In order to study the redox properties of the pristine samples and re-oxidized samples, temperature-programmed reduction (TPR) by H₂ was performed. For a better comparison, the diluted samples D-CuAl are investigated to keep the CuO amount constant in different solid samples (as described in the experimental section). For each sample, the total H₂ consumption calculated by the TPR profile is close to the amount required to fully reduce CuO to metallic Cu. As presented in **Figure S4**, the CuO loading amount is a key factor to determine the reduction features. For low loading samples (CuO loading below 0.6 mmol/100 m²), pristine CuAl samples show single reduction peaks, which can be attributed to the reduction of highly dispersed CuO

species.^{46, 50, 51} Interestingly, the peak shifts to lower temperature with the increasing the CuO loadings, indicating the reduction is easier to take place when the size of CuO species increase from single Cu²⁺ sites to clusters with several atoms. After re-oxidation in dry air, low loading CuAl-HO samples show two reduction peaks similar to the profiles of pristine high loading samples (**Figure S4**), which is related to the co-existence of both agglomerated and highly dispersed CuO species.^{27,32,33} Nevertheless, if re-oxidized by wet air (with moisture), the CuAl-HW samples show similar reduction features with pristine CuAl samples, only with the peak shift to lower temperatures. Considering that the reduction temperature of supported CuO species is related to their dispersion state, it appears that the H₂ reduction and dry air re-oxidation treatment can prompt the agglomeration of small CuO clusters and single Cu²⁺ sites, resulting in two reduction temperature in TPR profiles. Wet air re-oxidation treatment will partially recover these CuO species to their initial state, with a small number of CuO species mildly agglomerated and easily reduced. The profiles of differently treated D-04CuAl samples are listed in **Figure 3a** for a comparative purpose.

As the CuO loading exceeds 0.6 mmol/100 m², a new peak near 200-240 °C emerges with the increasing CuO loading, which can be assigned to the reduction of crystalline CuO species (see **Figure S4**).^{46, 50, 51} This matches well with XRD result that the amount of crystalline CuO species increases with the CuO loadings. The TPR reduction profiles for reduction-oxidation treated high loading samples (CuAl-HO and CuAl-HW) are similar to the pristine CuAl samples, regardless of the presence or the absence of H₂O during the oxidation treatments. In this case, the re-oxidation process seems to have limited influence on the redox behavior of crystalline CuO species.

The dispersion of CuO species during the reduction-oxidation process has also been studied by EPR spectroscopy. The total amounts of CuO species in all the tested samples are kept the same. As shown in **Figure 3b** and **Figure S5**, the EPR intensities of isolated Cu²⁺ species for CuAl-HO series are much lower than that of pristine CuAl series, indicating that CuO species are agglomerated after reduction by H₂ and re-oxidation in dry air. However, when the samples were re-oxidized in the presence of H₂O, the EPR intensity almost recover in all the samples, which further confirms the re-dispersion of CuO species during the re-oxidation process in the presence of H₂O. Besides, the influences of pretreatment are much more significant on CuAl samples with low CuO loading (≤ 0.2 mmol/100 m², see **Figure S5**), which suggests that the dynamic structural transformation mainly occurs on highly dispersed CuO species during the reduction-oxidation treatments.

Furthermore, the chemical states and coordination environment of CuO species in the 04CuAl samples have also been studied by XAFS. As shown in **Figure 3c**, the pristine 04CuAl sample shows a similar but different signature of X-ray absorption near edge structure (XANES) in comparison with CuO reference samples, indicating the 04CuAl sample should contain Cu²⁺ species. The differences in XANES spectrum shape are generally ascribed to the difference of the chemical environments of the Cu²⁺ compared to the reference sample, suggesting the highly dispersed nature and complex coordination environments of the Cu²⁺ species on γ -Al₂O₃ support.^{13, 25, 27, 52-55} The XANES spectra of the re-oxidized samples (see **Figure 3c**) are almost the same as the pristine 04CuAl sample, indicating the presence of Cu²⁺ species in all the samples. The presence of singly dispersed Cu²⁺ species has also been confirmed by the extended X-ray absorption fine structure (EXAFS) spectrum. As can be seen in **Figure 3d**, **Figure S6** and **Table S1**, the 04CuAl sample shows an intensity contribution at 1.9–2.0 Å, corresponding to Cu-

O coordination. Notably, there is a weak contribution at 2.9–3.0 Å, which can be ascribed to the second shell coordination of Cu-O-Cu species originated from the CuO_x clusters, as we have observed in the AC-STEM images in **Figure 2b and 2e**.^{45, 56} A higher contribution of the second-shell Cu-O-Cu can be observed in the 04CuAl-HO sample, indicating the presence of a larger number of CuO_x clusters compared to the pristine 04CuAl sample. When it comes to 04CuAl-HW, the Cu-O-Cu contribution has shown similar intensity with that of the pristine 04CuAl sample, which further suggests that wet air re-oxidation treatment will recover the agglomerated CuO species to their initial state.

Figure 3. (a) TPR profiles of pristine and differently treated D-04CuAl sample; (b) EPR spectra of pristine and differently treated D-04CuAl sample; (c) Cu K-edge XANES spectra of fresh and differently treated 04CuAl samples, and CuO reference; (d) Fourier-transforms of k^3 -weighted Cu K-edge EXAFS spectra of pristine and differently treated 04CuAl samples, and CuO reference.

In order to investigate the evolution of CuO dispersion state, we have also performed *in situ* XPS studies on the CuAl samples during the reduction-oxidation treatments. The XPS profiles of a series of CuAl samples are shown in **Figure S7-S8** and the surface atomic ratios of Cu/Al have

also been calculated. The profiles of differently treated 04CuAl samples are listed in **Figure 4a**. As discussed above, peaks at a binding energy of ~ 934.0 eV corresponds to Cu^{2+} species, while peaks at ~ 932.0 eV relate to Cu^0 or Cu^+ species.⁴¹ After reduction by H_2 , the peak at ~ 934.0 eV shifts to a lower binding energy, the satellite peak at ~ 942.5 eV vanishes and the intensity of $\text{Cu}2p_{3/2}$ peak significantly decreases, indicating that CuO species are fully reduced to metallic Cu, which is also proved by the complete reduction before 400°C according to the TPR profile in **Figure 3a**.⁵⁷ After re-oxidation with dry air, the intensity increases, but is still much lower than that of the initial state. When re-oxidized by wet air, the XPS profile has almost recovered to its initial state. As can be seen in **Figure S7**, other samples with CuO loading below $0.6\text{ mmol}/100\text{ m}^2$ have shown the same trend after different pretreatments. The result suggests that, for CuAl-H, Cu species can be fully reduced and agglomerated to metallic particles. For CuAl-HO, the metallic Cu particles are fully oxidized to CuO, which is in line with XAFS data. For CuAl-HW, full oxidation accompanied with nearly full re-dispersion occurs. Since the Cu/Al ratio of CuAl-HW is slightly lower than that of pristine CuAl, a small amount of CuO species in CuAl-HW may have kept the agglomerated state. This matches well with the deductions drawn from the TPR results.

Figure 4. (a) *In situ* XPS of Cu 2p_{3/2} region of pristine and differently treated 04CuAl sample; (b-g) are the high-resolution STEM images of 04CuAl sample after various treatments: (b, c) 04CuAl-H (d, e) 04CuAl-HO (f, g) 04CuAl-HW; (h) is a schematic illustration of the dynamic structural transformation of Cu species in 04CuAl sample.

Figure 5. (a-f) are the high-resolution STEM images of 01CuAl sample after various treatments. (a, b) 01CuAl-H (c, d) 01CuAl-HO (e, f) 01CuAl-HW. (g) is a schematic illustration of the dynamic structural transformation of Cu species in 01CuAl sample.

To obtain structural information of supported Cu species during various treatments at atomic resolution, the 04CuAl samples have been studied by AC-STEM. After reduction by H₂, a large number of Cu nanoclusters are formed in the 04CuAl-H sample (see **Figure 4b** and **4c**). The particle size of those Cu nanoclusters ranges from 0.4 to 1.2 nm with an average size of ~0.8 nm.

It should be mentioned that a small fraction of singly dispersed Cu atoms is still present in the 04CuAl-H sample. But the portion of singly dispersed Cu atoms is much less than the pristine 04CuAl sample, indicating the agglomeration of Cu atoms into Cu clusters during the H₂ reduction process. As discussed before, the reduced 04CuAl-H sample can be oxidized by dry air, giving to the 04CuAl-HO sample. As can be seen in **Figure 4d** and **4e**, a large number of subnanometric Cu clusters are still present in the 04CuAl-HO sample. The particle size of those subnanometric Cu clusters in the 04CuAl-HO sample is almost the same as in the 04CuAl-H sample, implying that the re-oxidation treatment of Cu clusters in dry air has a minor influence on the dispersion state of Cu species supported on γ -Al₂O₃. Interestingly, if the re-oxidation of reduced CuO clusters is carried out in the presence of water, the dispersion of Cu species changes. The AC-STEM images presented in **Figure 4f** and **4g** demonstrate that most of the Cu species exist as atomically dispersed Cu²⁺ species in the 04CuAl-HW sample with the presence of some subnanometric CuO clusters, which is similar to that of the pristine 04 CuAl (**Figure 2b** and **2e**). **Figure 4h** summarizes a significant yet not perfect agglomeration-redispersion of CuO_x species with medium loadings during the reduction-oxidation treatment.

For a clearer picture on the influence of CuO loading on the structural transformation of Cu species on γ -Al₂O₃ during redox treatments, the 01CuAl samples after reduction by H₂ and subsequent oxidation treatments have also been studied by HR-STEM. As can be seen in **Figure 5a** and **5b**, singly dispersed Cu species agglomerate into subnanometric Cu clusters after reduction by H₂. It should be noted that, as displayed in **Figure S9**, the Cu nanoclusters formed in the 04CuAl-H sample show a larger size than those formed in the 01CuAl-H sample (**Figure S10**). More importantly, the Cu nanoclusters in the 04CuAl-H sample exhibit more compact and ordered structures at the atomic level, which may further influence their physicochemical

properties. The Cu clusters formed in the 01CuAl-H sample are around 0.5 nm, basically containing 10-15 atoms and showing disordered structures at the atomic level. After a subsequent re-oxidation treatment in dry air, most of the Cu clusters remain on γ -Al₂O₃ support (see **Figure 5c** and **5d**). Interestingly, when the re-oxidation treatment occurs in the presence of H₂O, the re-dispersion of Cu clusters into singly dispersed Cu²⁺ sites is promoted. As presented in **Figure 5e** and **5f**, the 01CuAl-HW sample exhibit similar morphology as the pristine 01CuAl sample. As illustrated in **Figure 5g**, when the CuO loading is <0.2 mmol/100 m², the atomically dispersed Cu²⁺ sites can show almost complete reversible transformation between singly dispersed Cu²⁺ sites and subnanometric CuO clusters during reduction-oxidation treatments in the presence of H₂O.

As discussed above, the size distribution of Cu species in various CuAl samples is related to the CuO loading. The above spectroscopic and microscopic characterizations have clearly shown that highly dispersed Cu species can undergo a dynamic structural transformation during reduction-oxidation treatments. The difference for samples with higher CuO loading is, the redispersion during the wet oxidation treatment is not as significant as observed with samples with low CuO loading. In other words, the promoting role of water for the re-dispersion of CuO species is also related to the size of CuO clusters. When the CuO loading further increases to >0.7 mmol/100 m², a large number of CuO nanoparticles are present in the pristine CuAl sample and the size of those nanoparticles is insensitive to the reduction-oxidation treatments. As a consequence, their redox properties show minor changes during the reduction-oxidation treatments.

According to our experimental results, the dynamic structural transformation of supported Cu species is strongly related to their particle size. Based on AC-STEM images, the sintering of

singly dispersed Cu^{2+} species into CuO clusters is similar on various CuAl samples with different CuO loading, although the size of the formed Cu clusters may be different. For CuAl-H samples with low CuO loadings ($<0.2 \text{ mmol}/100 \text{ m}^2$), the size of the Cu clusters is mostly around 0.5 nm or below (see **Figure S10**), while those Cu clusters in the CuAl samples with higher CuO loadings shift to a larger size after reduced in H_2 . Specifically, a significant part of Cu clusters of $\sim 0.8 \text{ nm}$ with higher crystalline structure can be observed in the 04CuAl-H sample after H_2 reduction treatment (see **Figure S9**). Moreover, the redispersion of Cu clusters back to singly dispersed Cu^{2+} sites vary significantly among different samples. It has been revealed in the literature that redispersion of Pt species during oxidative treatment is related to their size. For smaller Pt species, the redispersion is more favorable than the big ones.^{6, 7} Herein, the redispersion behavior of subnanometric Cu clusters is also found to be quite sensitive to the particle size. From a mechanistic point of view, the redispersion of CuO clusters into singly dispersed atoms requires the extraction of Cu^{2+} ions from the crystalline lattice. For larger CuO clusters, due to the more packed arrangement of Cu^{2+} ions in the particles, higher energy may be needed. Small CuO clusters with less than 15 Cu atoms usually exhibit amorphous geometric structure, which should be relatively easier to be fragmented.

To understand the mechanism of this redispersion, a carrier-involved water-assisted dispersion pathway was proposed. According to the recent studies on the migration, agglomeration and dispersion of the supported metal species, both the support⁵⁸⁻⁶¹ and the reactants^{14, 31-33, 62-64} will participate in the dynamic transformation of supported metal species. For CuO/ $\gamma\text{-Al}_2\text{O}_3$ system in this work, we have found that wet air promotes the redispersion of agglomerated CuO_x clusters on $\gamma\text{-Al}_2\text{O}_3$. On the one hand, Cu^{2+} , according to previous reports, tends to diffuse into octahedral Al^{3+} vacancies on the $\gamma\text{-Al}_2\text{O}_3$ surface,^{65, 66} which could be the key for the confinement the Cu

atoms moving on the surface (see Figure S2 and S3). On the other hand, water molecules or hydroxyl groups are known as a ligand for the activation of $\text{Cu}^{\delta+}$. Compared with $\text{Cu}^{2+}\text{-}2\text{Z}$ (Z for the framework negative charge), it is computed by DFT methods that $[\text{Cu}(\text{OH})]^+\text{-Z}$ is easier to migrate under hydrothermal conditions (the Gibbs free energy for Cu^{2+} to detach via a hydrolysis process is 155 kJ/mol vs. 233 kJ/mol for the $\text{Cu}^{2+}\text{-}2\text{Z}$).⁶⁷ Moreover, based on AIMD simulations, the more H_2O molecules binding to the $\text{Cu}(\text{II})$ ions, the more mobile the $\text{Cu}(\text{II})$ structure becomes.²⁶

In summary, we propose a carrier-involved water-assisted dispersion mechanism. In the presence of water, Cu hydroxide species ($[\text{Cu}(\text{OH})_x \cdot y(\text{H}_2\text{O})]^{2-x}$) could be formed and they may migrate from the CuOx clusters to the octahedral Al^{3+} vacancies in the $\gamma\text{-Al}_2\text{O}_3$ support, leading to the redispersion of CuOx clusters into atomically dispersed Cu.

Figure 6. (a) Catalytic performance of differently pretreated 01CuAl and D-CuAl samples for NO reduction by CO at 350 °C; (b) Catalytic performance of differently pretreated 01CuAl and D-CuAl samples for NH₃-SCR at 425 °C. Note: For D-CuAl samples with higher CuO loading than 01CuAl, the catalyst was diluted with γ -Al₂O₃ to ensure the same CuO amount in the solid catalyst as the 01CuAl sample.

Catalytic behaviors of various CuO/ γ -Al₂O₃ catalysts. Based on the dispersion of CuO species in various CuAl samples and the dynamic transformation of CuO species during reduction-oxidation treatments, we can further study the catalytic properties of CuAl samples and try to correlate the structural-performance relationship of CuO species. Herein, two gas-phase reactions (NO reduction by CO and NH₃-SCR) are chosen as model reactions for deNO_x applications. The amounts of CuO species in all tested samples are kept the same by dilution of samples with higher Cu loadings.

As shown in **Figure 6a**, the pristine 01CuAl sample shows poor activity for NO+CO reaction at 350 °C. When the CuO loading increases, a significant increase of activity can be observed for the pristine CuAl catalysts, indicating that agglomerated CuO species are more active than the isolated CuO species for NO+CO reaction.

As discussed above, the size of the CuO species can be modulated by reduction-oxidation treatments. After reduction by H₂ and then oxidation by dry O₂, the activity of 01CuAl-HO sample is much higher than that of pristine 01CuAl. Moreover, we have also tested the activity of 01CuAl-HW and it shows a medium activity between pristine 01CuAl and 01CuAl-HO. Combining the results obtained before on the dispersion of CuO species after various treatments, it is implied that atomically dispersed Cu²⁺ sites show poor activity for NO+CO while agglomerated CuO clusters generated after reduction and subsequent oxidation by dry air are much more active, which is supported by the catalytic results obtained on other CuAl catalysts with higher CuO loading. On the one hand, as can be seen in **Figure 6a**, the activity difference between the pristine CuAl catalysts with CuO loading of 0.2-0.6 mmol/100 m² and the corresponding catalysts after reduction and subsequent oxidation by dry air (CuAl-HO) becomes less significant as the CuO loading increases. On the other hand, the catalytic performances of

re-dispersed samples (namely the CuAl-HW samples) are closer to that of the pristine samples when the CuO loading increases. For 10CuAl sample, the reduction-oxidation treatments have minor influences on the catalytic performance, which can be ascribed to the limited structural transformation of Cu species with relatively larger particle size during the reduction-oxidation treatments. These catalytic results indicate that agglomerated CuO species could be the active sites for NO+CO reaction while highly dispersed CuO species show poor activity for this reaction.²² To further explore the correlation between the dispersion of CuO species and their catalytic behavior, we also tested the light-off curve of D-04CuAl series for the product selectivity as well as the activity (See **Figure S11**). It should be mentioned that the major product of all samples is N₂ and the by-product is mainly N₂O. The selectivity for N₂ is usually lower at relatively low temperatures (~300 °C) than that of the catalyst at high temperatures (≥ 350 °C). This is ascribed to the limited redox activity of Cu^{δ+} species. According to previous reports,^{68,69} N₂O evolution is correlated with the presence of Cu⁺ sites, but the production of N₂ requires further reduced Cu^{δ+} or even Cu⁰ as active sites. The *in situ* reduction of CuO is easier to happen at high temperature, leading to higher selectivity for N₂. Moreover, based on the literature^{46, 70, 71} and the TPR results (see **Figure 3a**), agglomerated CuO can be reduced at lower temperature than highly dispersed Cu²⁺. This higher redox ability explains the higher activity and selectivity of D-04CuAl-HO, especially at low temperatures.

A major difference is observed when the selective catalytic reduction NO by NH₃ (NH₃-SCR) is used as the probe reaction. It has been widely reported in the literature that highly dispersed Cu²⁺ is the key to the activity and selectivity for NH₃-SCR reaction.^{25, 29} Due to the water and ammonia in the NH₃-SCR reaction environment, a large portion of agglomerated CuO can be redispersed at high temperatures. As displayed in **Figure 6b**, for pristine CuAl samples, the

influence of CuO loading is quite minor, especially for samples with low CuO loading (≤ 0.4 mmol/100 m²). When the loading of Cu increases to higher than 0.6 mmol/100 m², the activity drops down because of the formation of more CuO clusters and crystalline CuO in those samples, resulting in the decrease of atomically dispersed Cu²⁺ sites in the working catalysts. For the light-off curves of D-04CuAl, all samples exhibit the high activity and selectivity at ~ 425 °C (see **Figure S12**). At higher temperatures, however, CuO clusters can decrease the selectivity by oxidizing NO to NO₂ because of the higher redox ability, resulting in the relatively lower activity and selectivity of D-04CuAl-HO and D-04CuAl-HW at temperatures ≥ 450 °C for some agglomerated CuO particles that were newly formed or haven't been redispersed.

Since the geometric factor could have a significant effect on the performance of supported catalysts, it is found that water could tune the activity of CuO/ γ -Al₂O₃ catalysts by modulating the dispersion of Cu during the redox treatment. This progress occurs not only during the pretreatment but also in the catalytic processes (like NH₃-SCR).

CONCLUSIONS

In this work, we have demonstrated the dynamic evolution of supported CuO_x catalysts under reduction-oxidation treatments systematically. By spectroscopic and microscopic techniques, it is shown that water plays a key role in the control of the dispersion of CuO_x species during the redox treatments. With the addition of water, agglomeration and redispersion of CuO_x species on the alumina support modulated by reduction-oxidation treatments can be tuned significantly. Furthermore, the catalytic behavior of CuO species in deNO_x related reactions ($\text{CO}+\text{NO}$, NH_3 -SCR), which is closely associated with their dispersions, can be varied by redox and water treatment consequently. This work highlights the possibility to control their size distributions by post-treatments for desired reactions and the importance to identify the size of active CuO_x species for deNO_x reactions.

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Notes

Any additional relevant notes should be placed here.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

A .pdf file containing STEM images, TPR profiles, EPR and XPS spectra, EXAFS fittings is provided.

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