Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information for

Probing the existing state of Cu(II) in Cu-Al spinel catalyst using N_2O decomposition reaction with the aid of conventional characterizations

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1. Preparation of Cu_2O

The Cu_2O sample was prepared using similar glycothermal approach as reported for the preparation of CeO_2 in the literature.[1] After $Cu(NO_3)_2{\cdot}3H_2O$ was dissolved in the deionized water, ethylene glycol and propionic acid were added under stirring to form a uniform solution. The obtained mixed solution was then transferred into a Teflon lined stainless steel autoclave and aged at 180 °C for 200 min under static condition. After cooling to room temperature, the resulted suspension was centrifuged. The filter cake was washed with distilled water and the ethanol solution to remove the surface residual ionic and the organic solvent. The obtained product was dried at 80 °C in air, and XRD characterization confirmed the formation of Cu_2O. The sample was also tested in N_2O decomposition.

2. Results

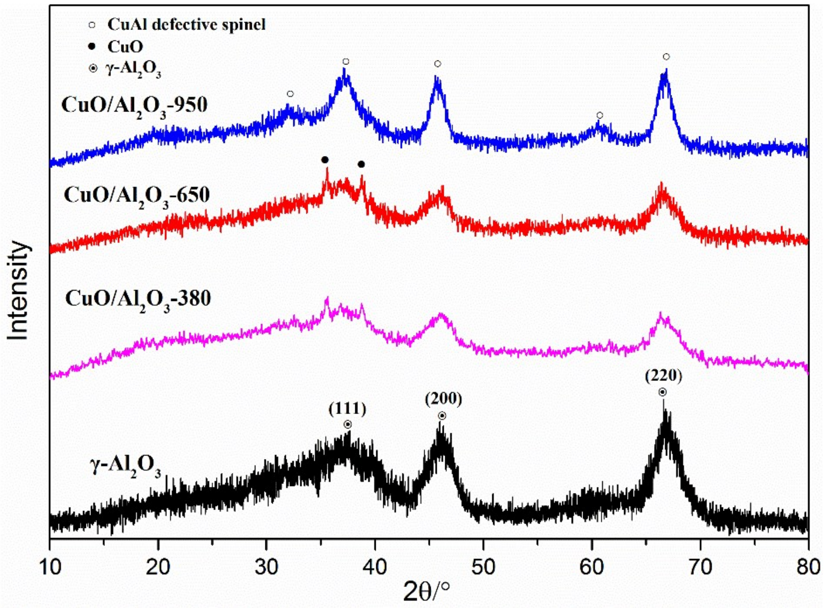

Figure S1. The XRD patterns of reference catalyst CuO/Al_2O_3 calcined at different temperatures and the reference sample γ-Al_2O_3

The XRD patterns of the reference catalyst CuO/Al_2O_3 and γ-Al_2O_3 sample are shown in Figure S1. The CuO phase can be detected in the reference sample CuO/Al_2O_3-380 and CuO/Al_2O_3-650, while the CuO phase disappears in CuO/Al_2O_3-950. The CuO diffraction peaks in CuO/Al_2O_3-650 is more sharply compared to CuO/Al_2O_3-380, indicating that the dispersion of CuO in the former is lower than that in the latter. It should be noted that the formation of CuAl spinel can also be discerned by comparing with γ-Al_2O_3 . It can be seen that γ-Al_2O_3 shows a stronger diffraction peak of (200) than (111), while CuO/Al_2O_3-380 and CuO/Al_2O_3-650 exhibit a higher peak of (111) than (200), suggesting that a small amount of CuO reacts with pseudo-boehmite to form the Cu-Al spinel phase. Apparently, more Cu-Al spinel is formed in CuO/Al_2O_3-

950. The formation of Cu-Al spinel was further evidenced by the following H_2-TPR characterization.

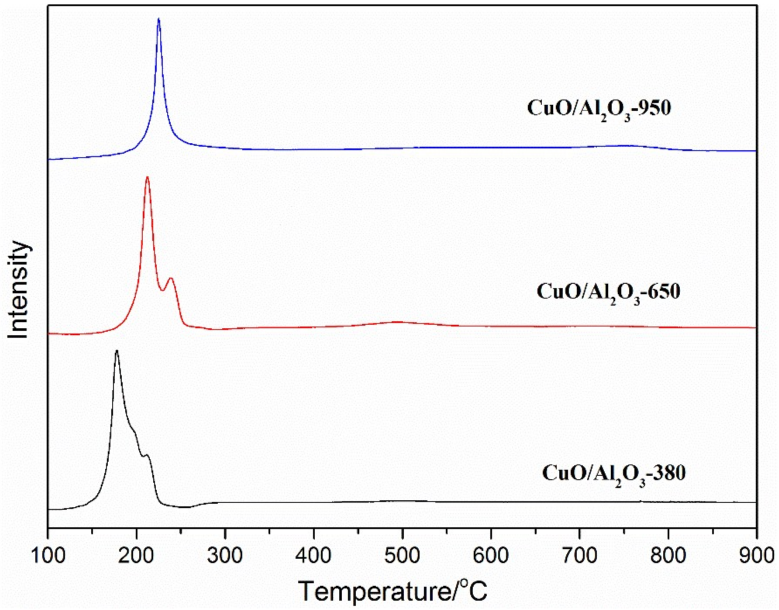

Figure S2. The TPR patterns of reference catalyst CuO/Al_2O_3 calcined at different temperatures

As shown in Figure S2, the reference samples, CuO/Al_2O_3-380, CuO/Al_2O_3-650 and CuO/Al_2O_3-950, exhibit a low temperature reduction peak attributed to NS-Cu(II) and a high temperature reduction peak ascribed to spinel type Cu(II). With increasing the calcination temperature from 380 to 950 °C, the reduction temperature of NS-Cu(II) gradually rises. Meanwhile, the peak area of the spinel type Cu(II) gradually increases, suggesting higher content of spinel, which is in good agreement with the above XRD data.

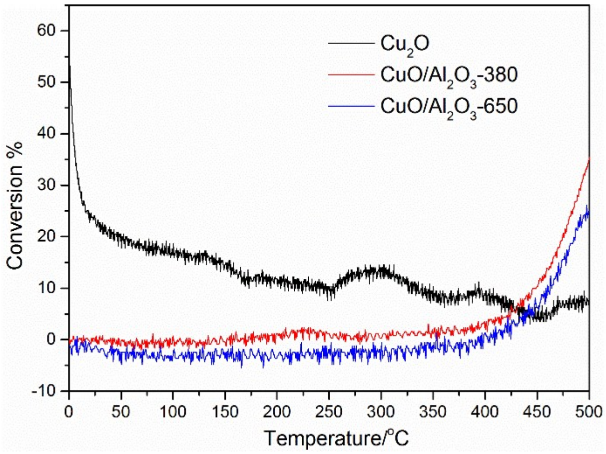

Figure S3 Temperature programmed conversion of N_2O over Cu_2O and CuO/Al_2O_3 calcined at different temperatures

The Cu_2O and CuO/Al_2O_3 calcined at different temperatures are applied in temperature programmed N_2O decomposition reaction, shown in Figure S3. The N_2O conversion for Cu_2O gradually declines with temperature rise. The initial high conversion is due to the Cu and the Cu_2O oxidization process by the N_2O as revealed by the following XRD pattern. The reference samples CuO/Al_2O_3-380 and CuO/Al_2O_3-650 show an increased activity with temperature rising, wherein the former shows a higher catalytic N_2O decomposition conversion than the latter.

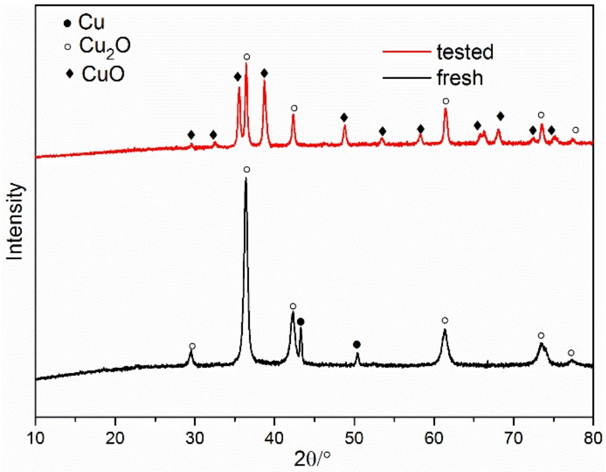

Figure S4 The XRD profile of Cu_2O, fresh (black line), the tested after N_2O decomposition reaction (red line)

The XRD profile of fresh and tested Cu_2O samples is shown in Figure S4. The fresh sample shows Cu_2O and metal Cu diffraction peaks. The calculated Cu_2O particle size is 28.2 nm and the metal Cu particle size is around 32.7 nm according to Scherrer formula. After reaction, the metal Cu is not detected, and the CuO phase is detected besides Cu_2O, indicating that the Cu_2O or Cu have been oxidized in the reaction process. The particle size of CuO and Cu_2O is around 25.3 nm and 28.1 nm, respectively.

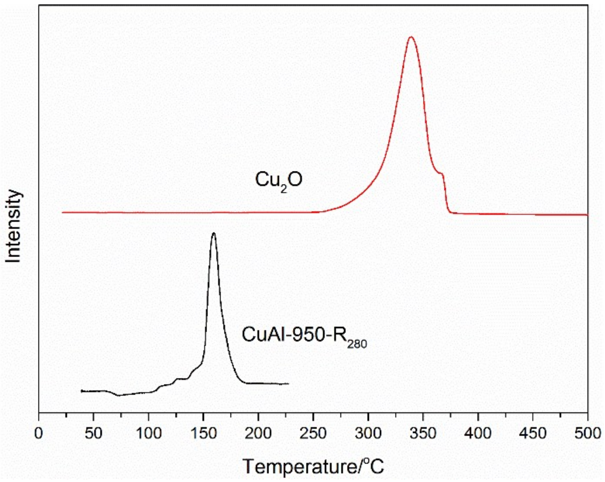

Figure S5 The TPR profile of the Cu_2O prepared by different methods. The black line represents the CuAl-950 catalyst reduced at 280 °C and then oxidized with N_2O at a low temperature (CuAl-950-R_{280}). The red line represents the Cu_2O prepared by the glycothermal approach.

The TPR profile in Figure S5 shows the Cu_2O in CuAl-950-R_{280} catalyst is reduced in a temperature range 100 °C -180 °C. However, the Cu_2O prepared by the glycothermal approach is to be reduced in a higher temperature range 250 °C-375 °C. The results demonstrate that the latter Cu_2O owns larger particles.

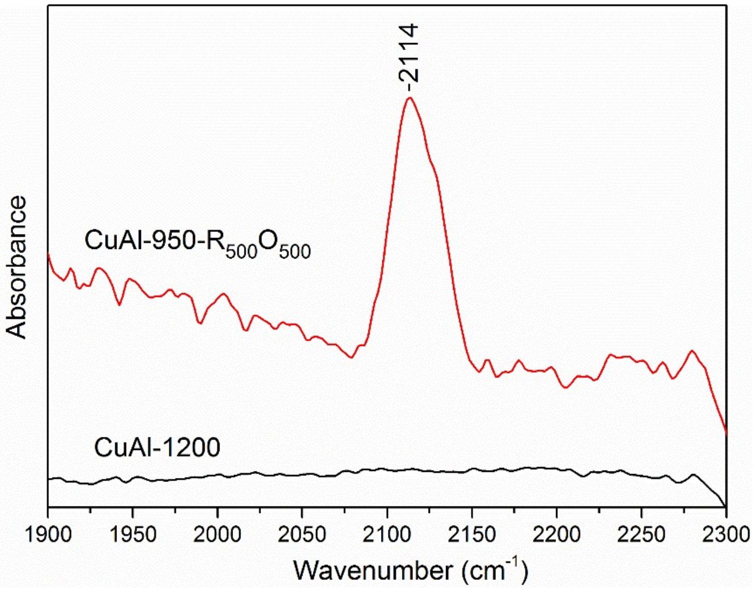

Figure S6. DRIFTS spectra of CO adsorbed at 300 K on the catalyst CuAl-1200 and CuAl-950-$R_{500}O_{500}$ separately after pretreated in Ar atmosphere at 500 °C for 30 min and then cooled to room temperature.

Figure S6 shows the IR spectra of CO adsorbed on the heat pretreated samples after exposure to CO followed by purging with Ar. The band at 2114 cm^{-1} remaining in the sample CuAl-950-$R_{500}O_{500}$, which is due to the C-O stretching modes of Cu^+-CO type carbonyls.[2, 3] For the sample CuAl-1200, the band essentially disappears.

References

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