## **Supporting information**

A heterogeneous single Cu catalyst of Cu atoms confined on the spinel lattice of  $MgAl_2O_4$  with good catalytic activity and stability for NO reduction by CO

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Figure S1. XRD patterns of 5%Cu-MgAl<sub>2</sub>O<sub>4</sub>.



Figure S2. N<sub>2</sub> adsorption and desorption isotherm (A) and pore size distribution (B) of the Cu<sub>1</sub>-MgAl<sub>2</sub>O<sub>4</sub> sample.



Figure S3.  $N_2$  adsorption and desorption isotherm (A) and pore size distribution (B) of the pure MgAl<sub>2</sub>O<sub>4</sub> sample.



Figure S4. The optimized geometry of the  $Mg_{11}CuAl_{24}O_{48}$  slab with the spinel structure of  $MgAl_2O_4$  and {311} surface.



**Figure S5.** CO-TPR profiles of the Cu<sub>1</sub>O<sub>1</sub>-MgAl<sub>2</sub>O<sub>4</sub> (a) and pure MgAl<sub>2</sub>O<sub>4</sub> (b) samples. The pure MgAl<sub>2</sub>O<sub>4</sub> sample has a strong negative peak around 75 °C and broad negative peaks above 240 °C due to the desorption of CO adsorbed on the pure MgAl<sub>2</sub>O<sub>4</sub> sample. No CO consumption peak is observed for the pure MgAl<sub>2</sub>O<sub>4</sub> sample, indicating that it cannot be reduced by CO. The Cu<sub>1</sub>O<sub>1</sub>-MgAl<sub>2</sub>O<sub>4</sub> sample has a strong negative peaks around 88 °C and broad negative peaks around 280 and 510 °C due to the desorption of CO adsorbed on the Cu<sub>1</sub>O<sub>1</sub>-MgAl<sub>2</sub>O<sub>4</sub> sample. In striking contrast to the pure MgAl<sub>2</sub>O<sub>4</sub> sample, the Cu<sub>1</sub>O<sub>1</sub>-MgAl<sub>2</sub>O<sub>4</sub> sample has a strong CO consumption peak around 366 °C, indicating that it is reduced by CO.



Figure S6. Geometry of a Cu<sub>32</sub> supercell with cubic structure of metallic copper.



**Figure S7.** Time course of NO conversion (A), N<sub>2</sub> yield (B), and N<sub>2</sub>O selectivity (C) of Cu<sub>1</sub>-MgAl<sub>2</sub>O<sub>4</sub> for NO reduction by CO at 400  $^{\circ}$ C at different space velocities of 60,000 (a) and 300,000 (b) mL g<sup>-1</sup><sub>catalyst</sub> h<sup>-1</sup>.



**Figure S8.** Time course of NO conversion (A), N<sub>2</sub> yield (B), and N<sub>2</sub>O selectivity (C) of Cu<sub>1</sub>-MgAl<sub>2</sub>O<sub>4</sub> for NO reduction by CO in the presence of water at 800 °C at a space velocity of 36,000 mL  $g^{-1}_{catalyst} h^{-1}$ .



**Figure S9**. Geometries of the initial states, transition states, and intermediates for NO reduction by CO on the  $CuMg_{11}Al_{24}O_{48}$  slab: Adsorbed CO (A), transition state of CO oxidation (B), and CO<sub>2</sub> intermediate (C) formed on the  $CuMg_{11}Al_{24}O_{47}$  slab with one oxygen vacancy. Adsorbed CO (D) and transition state of CO oxidation (E) on the  $CuMg_{11}Al_{24}O_{47}$  slab with one oxygen vacancy, and CO<sub>2</sub> intermediate (F) formed on the resultant  $CuMg_{11}Al_{24}O_{46}$  slab with two oxygen vacancies. Two adsorbed NO molecules (G) and transition state of  $N_2O_2$  decomposition to  $N_2O$  (H) on the  $CuMg_{11}Al_{24}O_{46}$  slab with two oxygen vacancy. Transition state of  $N_2O$  intermediate (I) formed on the resultant  $CuMg_{11}Al_{24}O_{47}$  slab with one oxygen vacancy and  $N_2$  intermediate of  $N_2O$  decomposition to  $N_2$  (J) on the  $CuMg_{11}Al_{24}O_{47}$  slab with one oxygen vacancy and  $N_2$  intermediate (K) formed on the resultant  $CuMg_{11}Al_{24}O_{47}$  slab with one oxygen vacancy and  $N_2$  intermediate (K) formed on the resultant  $CuMg_{11}Al_{24}O_{47}$  slab with one oxygen vacancy and  $N_2$  intermediate (K) formed on the resultant  $CuMg_{11}Al_{24}O_{47}$  slab with one oxygen vacancy and  $N_2$  intermediate (K) formed on the resultant  $CuMg_{11}Al_{24}O_{47}$  slab with one oxygen vacancy and  $N_2$  intermediate (K) formed on the resultant  $CuMg_{11}Al_{24}O_{47}$  slab with one oxygen vacancy and  $N_2$  intermediate (K) formed on the resultant  $CuMg_{11}Al_{24}O_{47}$  slab with one oxygen vacancy and  $N_2$  intermediate (K) formed on the resultant  $CuMg_{11}Al_{24}O_{47}$  slab with one oxygen vacancy and  $N_2$  intermediate (K) formed on the resultant  $CuMg_{11}Al_{24}O_{48}$  slab.



Figure S10. FTIR spectra of 10 vol%  $N_2O/He$  on the Cu<sub>1</sub>-MgAl<sub>2</sub>O<sub>4</sub> sample.