Supporting information

A heterogeneous single Cu catalyst of Cu atoms confined on the spinel lattice of MgAl₂O₄ with good catalytic activity and stability for NO reduction by CO.

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Figure S1. XRD patterns of 5%Cu-MgAl₂O₄.

Figure S2. N₂ adsorption and desorption isotherm (A) and pore size distribution (B) of the Cu₁-MgAl₂O₄ sample.
Figure S3. N$_2$ adsorption and desorption isotherm (A) and pore size distribution (B) of the pure MgAl$_2$O$_4$ sample.

Figure S4. The optimized geometry of the Mg$_{11}$Cu$_{24}$O$_{48}$ slab with the spinel structure of MgAl$_2$O$_4$ and {311} surface.
Figure S5. CO-TPR profiles of the Cu$_{1}$O$_{1}$-MgAl$_{2}$O$_{4}$ (a) and pure MgAl$_{2}$O$_{4}$ (b) samples. The pure MgAl$_{2}$O$_{4}$ 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$_{2}$O$_{4}$ sample. No CO consumption peak is observed for the pure MgAl$_{2}$O$_{4}$ sample, indicating that it cannot be reduced by CO. The Cu$_{1}$O$_{1}$-MgAl$_{2}$O$_{4}$ sample has a strong negative peak around 88 °C and broad negative peaks around 280 and 510 °C due to the desorption of CO adsorbed on the Cu$_{1}$O$_{1}$-MgAl$_{2}$O$_{4}$ sample. In striking contrast to the pure MgAl$_{2}$O$_{4}$ sample, the Cu$_{1}$O$_{1}$-MgAl$_{2}$O$_{4}$ sample has a strong CO consumption peak around 366 °C, indicating that it is reduced by CO.

Figure S6. Geometry of a Cu$_{12}$ supercell with cubic structure of metallic copper.
Figure S7. Time course of NO conversion (A), N\textsubscript{2} yield (B), and N\textsubscript{2}O selectivity (C) of Cu\textsubscript{1}-MgAl\textsubscript{2}O\textsubscript{4} for NO reduction by CO at 400 °C at different space velocities of 60,000 (a) and 300,000 (b) mL g\textsuperscript{-1}\textsubscript{catalyst} h\textsuperscript{-1}.
Figure S8. Time course of NO conversion (A), N\textsubscript{2} yield (B), and N\textsubscript{2}O selectivity (C) of Cu\textsubscript{1}-MgAl\textsubscript{2}O\textsubscript{4} for NO reduction by CO in the presence of water at 800 °C at a space velocity of 36,000 mL g\textsuperscript{-1}\text{catalyst h}\textsuperscript{-1}.
Figure S9. Geometries of the initial states, transition states, and intermediates for NO reduction by CO on the CuMg₁₁Al₂₃O₄₈ slab: Adsorbed CO (A), transition state of CO oxidation (B), and CO₂ intermediate (C) formed on the CuMg₁₁Al₂₃O₄₇ slab with one oxygen vacancy. Adsorbed CO (D) and transition state of CO oxidation (E) on the CuMg₁₁Al₂₃O₄₇ slab with one oxygen vacancy, and CO₂ intermediate (F) formed on the resultant CuMg₁₁Al₂₄O₄₆ slab with two oxygen vacancies. Two adsorbed NO molecules (G) and transition state of N₂O₂ decomposition to N₂O (H) on the CuMg₁₁Al₂₄O₄₆ slab with two oxygen vacancies, and N₂O intermediate (I) formed on the resultant CuMg₁₁Al₂₃O₄₇ slab with one oxygen vacancy. Transition state of N₂O decomposition to N₂ (J) on the CuMg₁₁Al₂₃O₄₇ slab with one oxygen vacancy and N₂ intermediate (K) formed on the resultant CuMg₁₁Al₂₃O₄₈ slab.
Figure S10. FTIR spectra of 10 vol% N$_2$O/He on the Cu$_2$-MgAl$_2$O$_4$ sample.