

ARTICLE

Supplementary Information

In all experiments the catalysts were first heated at (400 °C for DR UV-Vis and 550 °C for SO₂ uptake and catalytic testing) in 10% O₂/N₂ flow and left at this temperature for 1 hour. The following steps are described for the four different procedures:

- Cooling in 10% O₂/N₂ flow at 200 °C, resulting in the formation of framework coordinated Cu^{II} sites (fw-Cu^{II}).
- 1% H₂/N₂ flow at 400 °C for 1 hour, followed by cooling in the same atmosphere to 200 °C, resulting in the formation of framework coordinated Cu^I sites (fw-Cu^I).
- Cooling in 10% O₂/N₂ flow at 200 °C, followed by 20 minutes N₂ purge and subsequent exposure to NO/NH₃ (500 ppm/600 ppm, rest N₂), resulting in the formation of 'mobile' [Cu^I(NH₃)₂]⁺ complex.
- The same procedure as in c), followed by N₂ purge and exposure to 10%O₂/N₂ for 30 min, resulting in the formation of [Cu^{II}₂(NH₃)₄O₂]²⁺ complexes.

Then subsequently the catalysts were exposed to 50 ppm SO₂/N₂ followed by the DR UV-Vis experiments and 100 ppm SO₂/N₂ for SO₂ uptake and catalytic testing measurements at 200 °C.

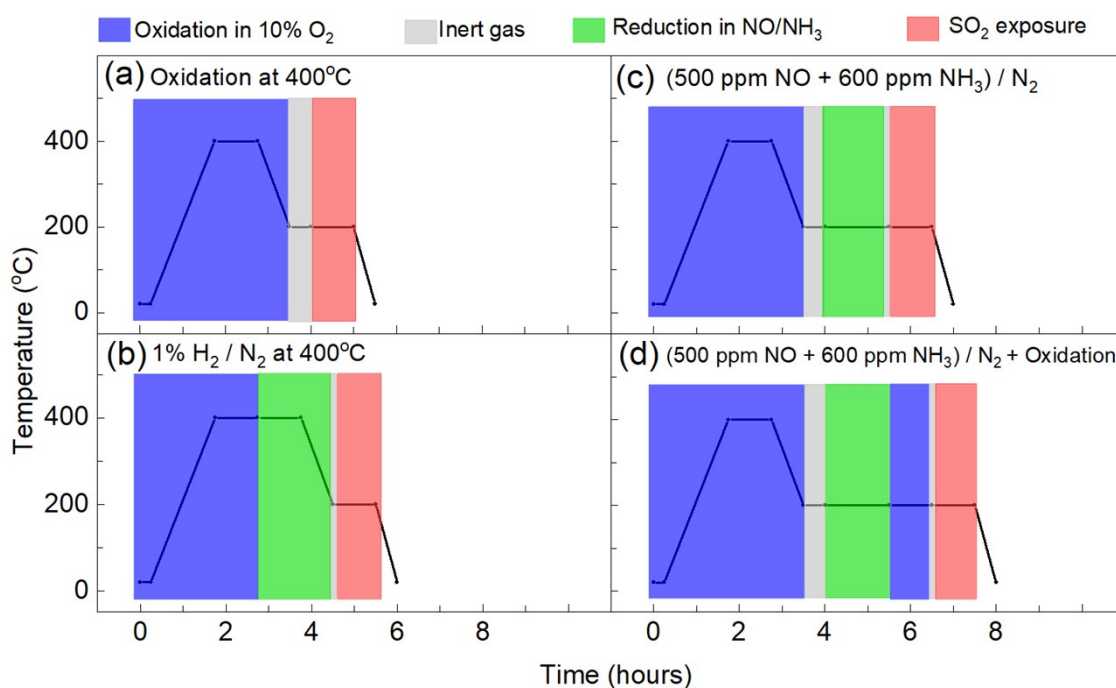


Fig. S 1 Schematic representation of the four procedures carried out to obtain (a) fw-Cu^{II}, (b) fw-Cu^I, (c) [Cu^I(NH₃)₂]⁺ complexes and (d) [Cu^{II}₂(NH₃)₄O₂]²⁺ complexes, and subsequent exposure to SO₂/N₂.

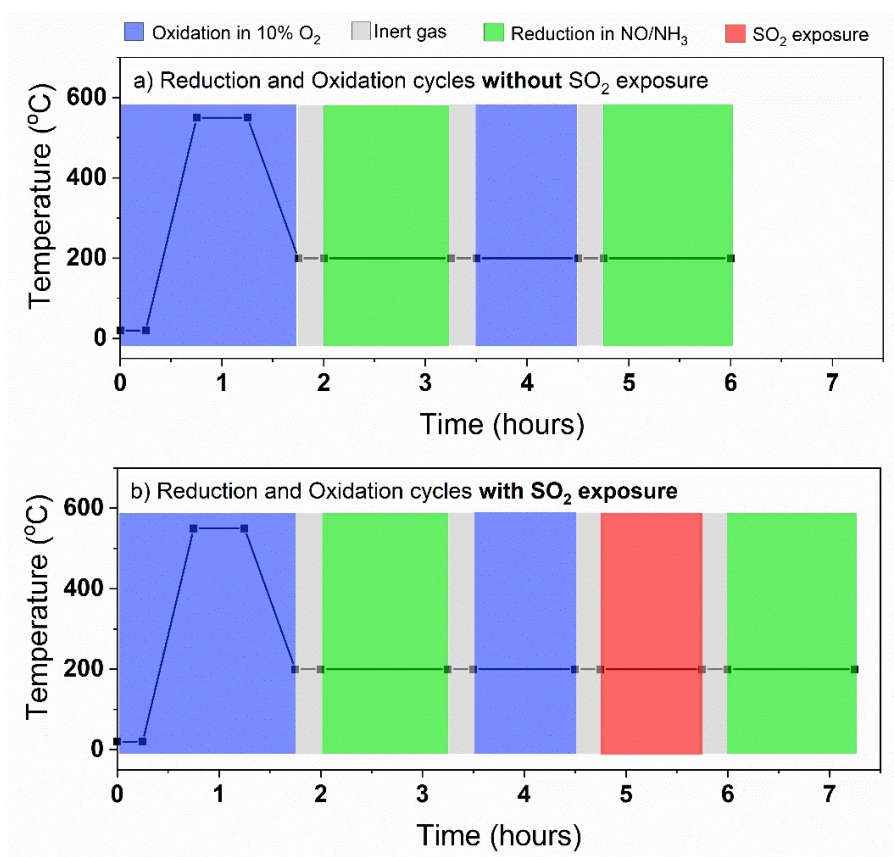


Fig. S 2 Schematic representation of oxidation and reduction cycles a) without SO₂, and b) with SO₂ at 200 °C.

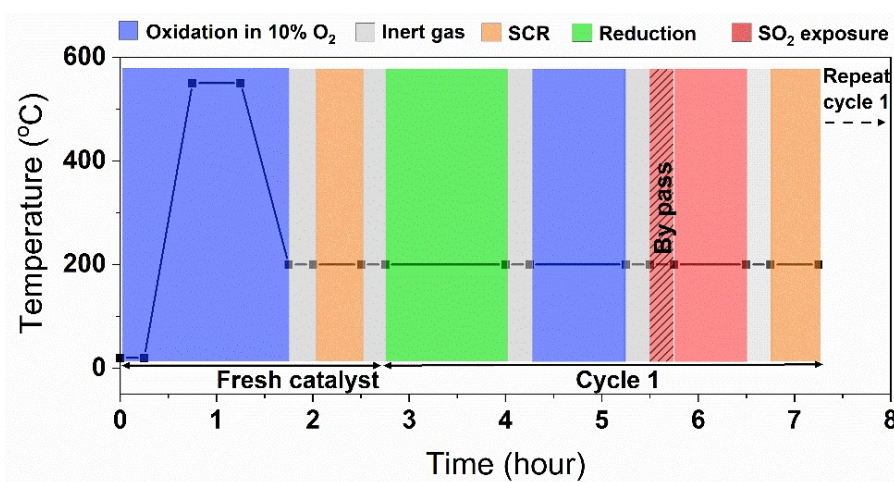


Fig. S 3 Schematic representation of repeated SO₂ exposure procedure to measure SO₂ uptake during SO₂ exposure and deactivation.

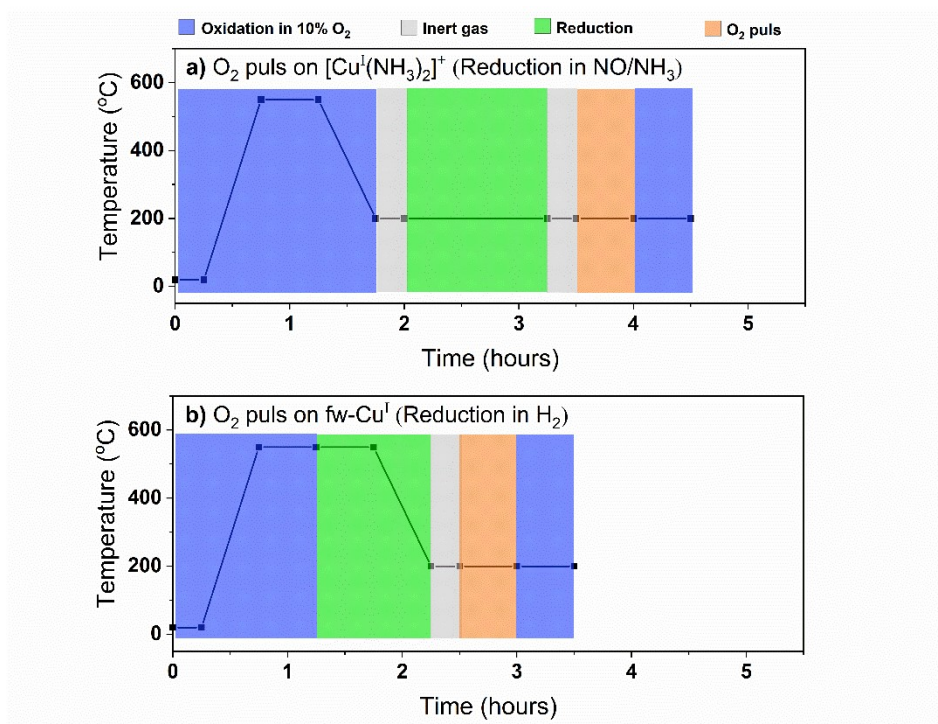


Fig. S 4 Schematic representation of O₂ pulse procedures on a) [Cu^I(NH₃)₂]⁺ and b) fw-Cu^I at 200 °C.