Scientists overcome NH3 synthesis shortcomings

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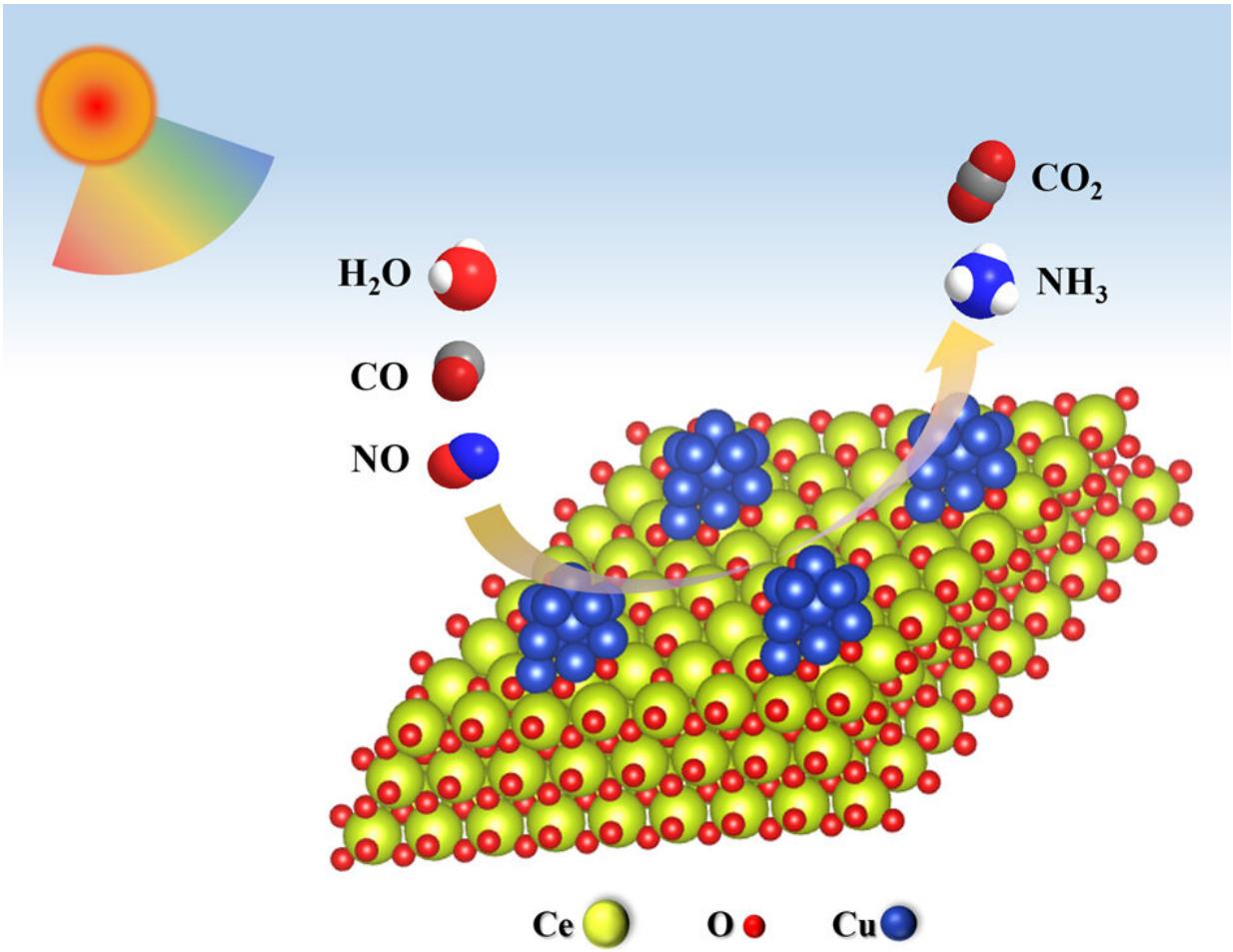

NH_3 is not only the key chemical raw material for the industry but also a carbon-free fuel and mobile carrier of renewable energy. In the NO-CO-H2O reaction, NO is reduced to NH_3 by CO and H_2O over Cu/CeO_2 under mild conditions. The visible-light-induced local surface plasmon resonance (LSPR) effect of Cu promotes the reactivity and selectivity of NH_3. Credit: Chinese Journal of

NH_3 is not only the key chemical raw material for the industry but also a carbon-free fuel and mobile carrier of renewable energy in the future. So far, industrial NH_3 synthesis is still dominated by the traditional Haber-Bosch reaction, which requires high temperatures of 300–500 ºC and pressures of 200–300 atm.

To overcome these shortcomings, Nanba et al. have designed the NO-CO-H_2O reaction system. In this reaction, NO was used as the raw material and reduced to NH_3 by H_2O and toxic gases CO. The reaction equation is as follows: $NO + 2.5CO + 1.5H_2O \rightarrow NH_3 + 2.5CO_2$ ($\Delta H_{298.15K}$= -414.86 kJ·mol^{-1})

Recently, their research found that the NO-CO-H_2O reaction can be approximately decomposed into a series reaction of WGSR of CO-H_2O and reduction of NO-H_2. The results were published in the *Chinese Journal of Catalysis*.

When the incident photon frequency of incident light matches the vibration frequency of noble metal nanoparticles, the nanoparticles have strong absorption of photon energy and local surface plasmon resonance (LSPR) occurs. The metal with the LSPR effect can excite high-energy hot electrons and holes, which helps to activate the reactants, thus reducing the reaction energy and increasing the reaction rate. As a rare non-noble metal with an LSPR effect, Cu has been widely used in CO hydrogenation reactions.

Cu/CeO_2 was prepared by a simple wet impregnation method and the reactivity of NO reduction to NH_3 by CO in a photothermal synergistic system was studied. As expected, high activity was obtained over

Cu/CeO_2 under visible light irradiation. The LSPR effect of Cu nanoparticles can increase the NH_3 yield under mild conditions.

Recently, a research team led by Prof. Wenxin Dai from Fuzhou University, China, reported a photothermal catalytic system comprising Cu/CeO_2 that was applied to the reaction between NO, CO and H_2O for the production of NH_3 under visible-light irradiation. High NO conversion (94.4%) and NH_3 selectivity (66.5%) were achieved over Cu/CeO_2 in the presence of H_2O at 210°C. Visible light further improved the conversion of NO (97.7%) and selectivity for NH_3 (69.1%).

The quasi-situ EPR and in-situ DRIFTS results indicated that CO initially reacts with H_2O to form an HCO_3^* intermediate, which then decomposes into CO_2 and activated H^*. Finally, NO reacts with activated H^* to produce NH_3. The localized surface plasmon resonance effect of Cu nanoparticles induced by visible light promotes the decomposition of HCO_3^* to CO_2 and H^*, while regenerating oxygen vacancies (OVs, H_2O activation sites) at the CeO_2 sites, resulting in enhanced NH_3 production.

More information: Xinjie Song et al, NH3 synthesis via visible-light-assisted thermocatalytic NO reduction by CO in the presence of H2O over Cu/CeO2, *Chinese Journal of Catalysis* (2023). DOI: 10.1016/S1872-2067(23)64439-0

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