Intensification of the low-temperature RWGS activity of copper ceria catalysts enabled by visible light

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Highlights

- Visible light accelerates the CO rate up to 57 times compared to thermal conditions in dark.
- Wavelengths shorter than 450 nm are most effective for boosting CO rate.
- Reaction mechanism changes during illumination.
- Most abundant surface species (CO_3^{2-} and HCOO) hydrogenate and dissociate faster under illumination.

1. Introduction

Strategies for CO_2 conversion into added value chemicals have garnered attention as essential pathways toward carbon neutrality.[1] CO_2 hydrogenation to hydrocarbons (Fischer-Tropsch synfuels or methane) and different alcohols, or to CO via the reverse water gas shift (RWGS) reaction are in the center of research as possibilities for large scale carbon capture and utilization (CCU).[2] Light-assisted catalysis is a promising approach for accelerating the thermally driven catalytic Reverse Water Gas Shift (RWGS) reaction, which converts CO_2 and H_2 into valuable CO.[3] This contribution analyzes mechanistic origins of visible light accelerated CO formation during the RWGS reaction using copper-based catalysts supported on titanium doped ceria nanorods.

2. Methods

CeO_2 nanorods, doped with titanium (0.5 mol.%) and decorated with 1, 3, 8 and 30 wt.% of copper were synthesized.[4] Catalytic tests and kinetic analysis were performed in a Harrick reaction chamber in the temperature range of 210-320°C. During the light-assisted experiments, the catalysts were illuminated with white light, Schott KL2500 LED source (visible light; λ = 400-700 nm), 770 mW cm^{-2}. In addition to N_2 sorption, XRD and SEM-TEM microscopy, Raman, *in-situ* UV-Vis and steady-state and time-resolved transient DRIFTS were performed on illuminated samples.

3. Results and discussion

When comparing the effect of copper content (1, 3, 8 and 30 wt. %) on CO rates, the following trend in catalytic activity was observed: 3Cu-CeTi > 8Cu-CeTi ≈ 1Cu-CeTi > 30Cu-CeTi. Illuminating the 3Cu–$CeTiO_2$ catalyst with 770 mWcm^{-2} of visible light resulted in a CO rate, which was up to 57-times higher than that under purely thermal conditions at identical catalyst temperature of 210°C.

Catalyst illumination with wavelengths shorter than 450 nm triggers simultaneous photoexcitation of the Ti doped CeO_{2-x} support and Cu nanoparticles via inter and intraband transitions. This accelerates the RWGS reaction approximately twofold more, compared to excitation of the copper phase alone (Figure 1A). Simultaneous photoexcitation of copper and ceria phases activates the spatially segregated reaction intermediates (HCOO* and CO_3* on ceria support, H* on copper), which enables efficient photon utilization to drive the photocatalytic CO_2 hydrogenation under mild conditions, unattainable with thermal catalyst excitation.

Furthermore, the apparent activation energy (Ea) for CO formation decreased drastically from 92 to 26 kJ mol^{-1} during the light-assisted reaction, revealing a change of the reaction mechanism and lowered energetics of the rate-determining step, Figure 1B.

The changes in Ea and reaction orders upon illumination (0.36 → 0.75 for CO_2 and 0.99 → -0.63 for H_2, Figure 1C) and wavelength-dependent CO rate suggest that the improved catalyst reactivity under illumination has a light induced origin. Considering that CO_2 reaction order under illumination increases notably, while that for H_2 assumes a negative value, the RDS under the light-assisted conditions is likely related to abundance of surface adsorbed CO_2 and CO_2 reactivity, either through the formate generation step (CO_2+H→ HCOO), carbonate decomposition step (CO_3*+H* →HCOO*+ O*), or carboxylate species formation through altered hydroxyl reactivity. Transient DRIFTS analysis under dark and illuminated conditions showed that the initial decay rate of characteristic carbonates and formates on the illuminated catalysts are 1.5 to 4.2-fold higher compared to dark, which reveals a positive effect of light on their removal and consequently, their increased reactivity. Control experiments ruled out the existence of redox (Mars-van Krevelen) reaction mechanism under dark or light-assisted conditions.

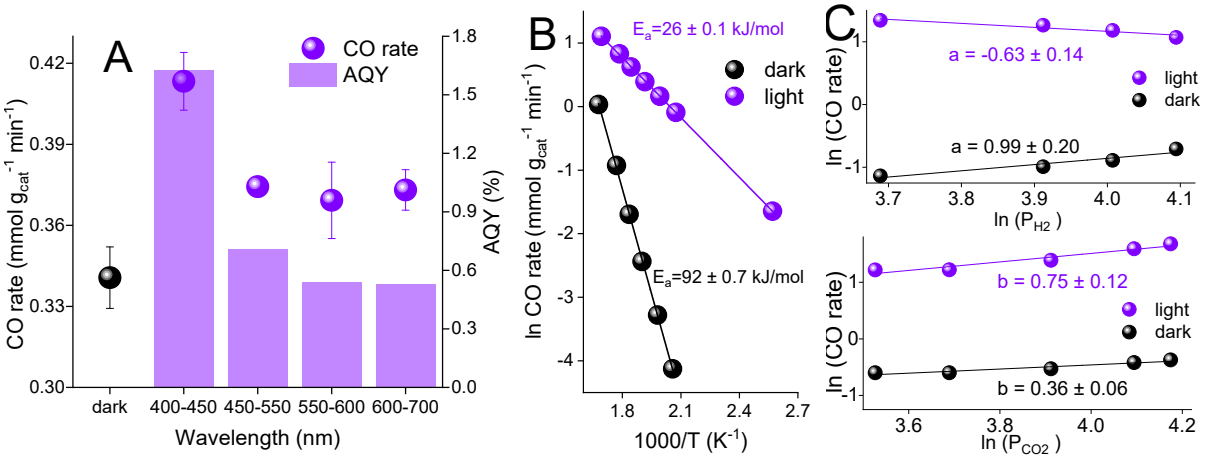

Figure 1. A) Wavelength dependent CO rate and Apparent Quantum Yield values for the 3Cu–$CeTiO_2$ catalyst at 270°C and irradiance of 230 mW cm^{-2}. B)) Apparent activation energy values (E_a) under dark and light-assisted RWGS conditions. C) CO_2 and H_2 reaction orders during dark and light assisted RWGS reaction.

4. Conclusions

This study demonstrates the positive impact of visible light on the activity of copper/ceria catalysts in the RWGS reaction.[4] Small copper loading (3 wt.%) produces the most active photocatalyst, suggesting the Cu/$CeTiO_{2-x}$ interface as the reactive perimeter. The reaction orders, Ea and wavelength dependent CO rate suggest the improved catalyst reactivity under illumination have a light-induced origin. Simultaneous photoexcitation of copper and ceria phases activates the spatially segregated reaction intermediates (HCOO* and CO_3* on ceria support, H*on copper) which enables efficient photon utilization to drive the photocatalytic CO_2 hydrogenation under mild conditions, unattainable with thermal catalyst excitation. Hydrogen dissociation is greatly improved upon illumination which enables the use of equimolar H_2/CO_2 or CO_2 rich feed streams for maximal CO rates. More effective CO_2 dissociation pathways via bidentate carbonate and formate intermediates contribute to better performance of the Cu-CeTi catalyst.

References

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Keywords
Cu/CeO_2 catalyst, CO_2 hydrogenation, *in-situ* spectroscopy, reaction mechanism, light-assisted catalysis.