Utilization of visible light in the Reverse Water Gas Shift reaction over $Cu/Ce_x(Ti_{1-x})O_2$ catalyst

Miha Okorn[1,2], Kristijan Lorber[1] and Petar Djinović[*1,2]
[1]*National Institute of Chemistry, Hajdrihova 19, Ljubljana, Slovenia.*
[2] *University of Nova Gorica, Vipavska 13, Nova Gorica, Slovenia.*
** petar.djinovic.si*

Significance and Relevance

The $Cu/Ce(Ti)O_2$ nanorod catalysts demonstrate significant potential for the light-assisted conversion of CO_2 to CO. During the light-assisted reaction, the activation energy (E_a) decreased substantially, leading to a significant increase in the CO formation rate and apparent change in the reaction mechanism compared to the thermally driven reaction. Furthermore, this contribution will present our latest research on catalyst structural characterization and in-situ spectroscopic analysis to better understand the influence of visible light on the reaction mechanism of the Reverse Water-Gas Shift (RWGS) reaction.

Preferred and 2nd choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization and CO_2 utilization and recycling
Preferred presentation: Oral preferred or short oral

Introduction and Motivations

The Reverse Water Gas Shift (RWGS) reaction presents an intriguing pathway for reducing CO_2 to valuable CO using renewable H_2. [1] Light-assisted catalysis, which synergistically combines thermal and light energy, offers a promising approach to accelerate the RWGS reaction. Ceria-based catalysts have gained a lot of interest in the CO_2 conversation processes, particularly in the form of nanorods which demonstrate higher catalytic activity among the different CeO_2 morphologies. [2] Modifying the CeO_2 nanorods with specific oxides like TiO_2 (a known photocatalyst)[3] and copper (with its unique plasmonic properties)[4] could potentially benefit the photo-thermal RWGS reaction by optimizing the absorption and utilization of visible light, improving surface properties of the support, forming additional active sites for H_2 and CO_2 activation, consequently leading to final CO formation. This approach can significantly reduce the energy input required for the traditional RWGS reaction while increasing CO_2 conversion and subsequent CO formation.

Materials and Methods

We synthesized Ti-doped (2 mol.%) CeO_2 nanorods as support and then deposited 1, 3, 8 and 30 wt.% of copper by wet impregnation. Using only visible light, we were able to compare thermal and light-assisted performance of the catalyst. The experiments were conducted in a fixed-bed reactor, where the analyzed temperature range was 200-320 °C at ambient pressure and the total flow rate of inlet gas mixture (CO_2/H_2 =1/1) was kept constant at 30 ccm during both thermal and light-assisted processes. Detailed characterization included SEM, XRD as well as *in-situ* UV-Vis and transient DRIFT spectroscopy for analysis of the catalysts optical absorption, oxygen defects and surface species in dark and under light-assisted conditions.

Results and Discussion

XRD analysis revealed that initial titanium doping expanded the CeO_2 crystal lattice due to the inclusion of Ti^{4+} ion into the CeO_2 crystal lattice, while Cu nanoparticles were dispersed on the surface of the support. Catalytic experiments demonstrated that all titanium-doped catalysts (xCu-CeTi) exhibited higher CO formation rates (R_{CO}) than undoped CeO_2 catalysts during light-assisted reactions (Figure 1A), suggesting a synergetic effect of titanium addition to CeO_2 nanorods and visible light. The catalyst containing 3 wt.% of Cu displayed the highest catalytic activity in both dark and light-assisted

conditions. As shown in Figure 1B, temperature dependent experiments indicated an increase in the activity of the 3Cu-CeTi catalyst with temperature, without any sings of deactivation under either reaction conditions. The catalyst shows no catalytic activity below 213 °C in dark, while significant activity (0.24 mmol CO/g_{cat}*min, catalyst temperature of 116 °C) was observed under light-assisted reaction without additional electric heating. Additionally, Arrhenius plots for the 3Cu-CeTi catalyst (Figure 1C) show a substantial decrease in apparent activation energy upon illumination, from 92 to 26 kJ/mol, indicating an alteration in the energetics of the rate-determining step of the RWGS reaction. Wavelength dependent experiments revealed that simultaneous excitation of copper and ceria support result in apparent quantum yields that are about two times higher compared to excitation of copper phase. Furthermore, transient operando DRIFTS experiments showed that illumination accelerates carbonate hydrogenation (to formate), and hydrogen-assisted formate dissociation to CO and H_2O, revealing the underlying origins of accelerated CO rate.

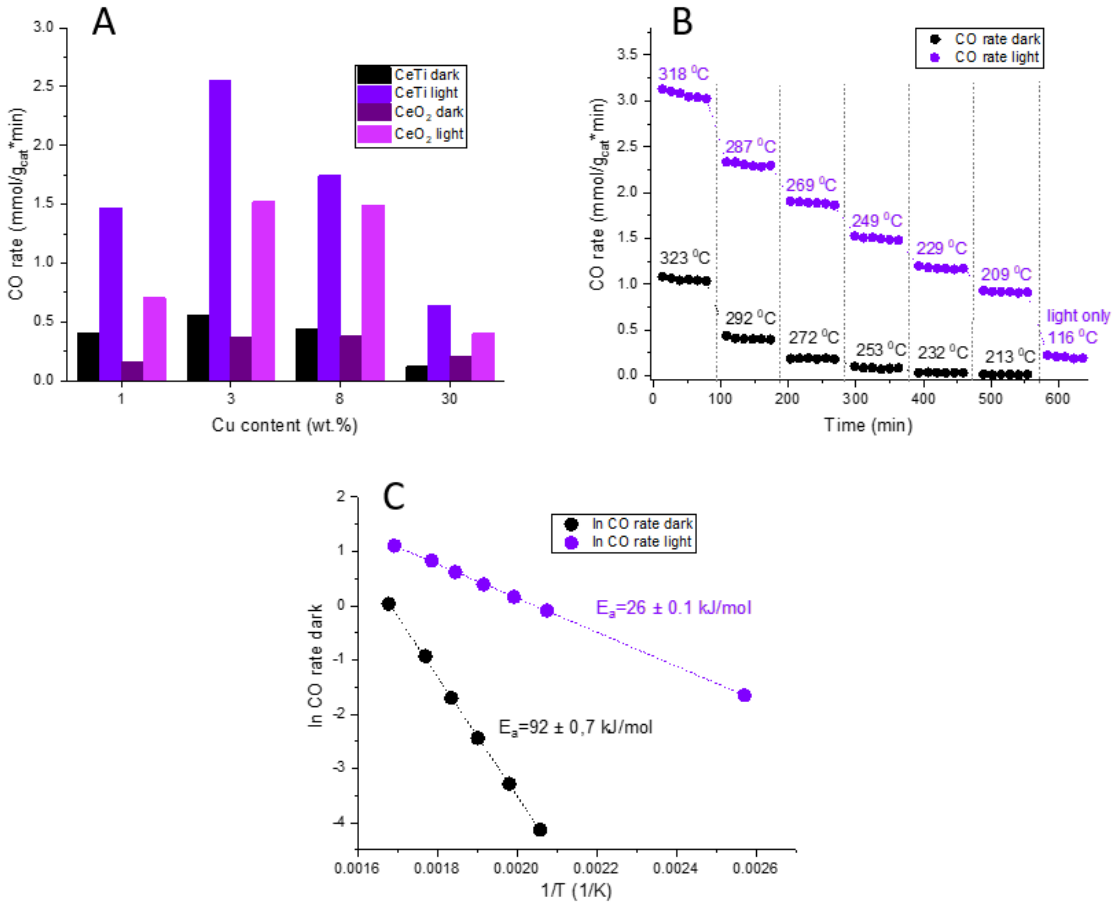

Figure 1: A) CO rate comparison under thermocatalytic and light-assisted conditions of different Cu loadings deposited on CeTi and CeO_2 supports using H_2/CO_2 feed ratio of 1/1 at 300 °C. B) Temperature dependence of the CO rate over the 3Cu-CeTi catalyst under dark and light-assisted conditions. C) Apparent activation energies under dark and light-assisted conditions.

References

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