

THERMAL AND VISIBLE LIGHT-ASSISTED CO₂ HYDROGENATION TO CO OVER AN INDUSTRIAL COPPER BASED CATALYST

Giovanni Cardolini Rizzo¹, Miha Okorn^{2,3}, Kristijan Lorber³, Nataša Novak Tušar^{2,3} and Petar Djinović^{2,3}

¹Politecnico di Torino, Corso Duca degli Abruzzi 24, Torino, Italy

²National Institute of Chemistry, Hajdrihova 19, Ljubljana, Slovenia

³University of Nova Gorica, Vipavska 13, Nova Gorica, Slovenia

E-mail: petar.djinovic@ki.si

ABSTRACT

Photo-thermal conversion of carbon dioxide into carbon monoxide (RWGS reaction) under mild conditions over suitable (photo)catalysts is attractive for production of petrochemical platform chemicals with minimal involvement of fossil fuel energy. In this contribution, we analyze a commercial Cu-ZnO-Al₂O₃ catalyst (HiFuel R120™) for its ability to act as photo-catalysts in RWGS reaction. By using a combination of visible light and thermal energy to drive the reaction, wavelength dependent catalytic studies and kinetic analysis, we confirmed that photons enable strong acceleration of CO formation. Notable differences in reaction mechanism were observed and corroborated with *in-situ* DRIFT spectroscopic data. This work reveals that commercial catalysts that contain components which absorb and utilize visible light can be used without any chemical modifications in photo-thermal catalysis with substantial benefits compared to established, thermally driven catalytic reactions.

Key words: CO₂ conversion, copper, catalysis, reaction mechanism, light-assisted catalysis

INTRODUCTION

The CO₂ hydrogenation reaction to CO (CO₂ + H₂ ↔ CO + H₂O, ΔH_r= 50 kJ/mol) is of particular interest due to direct use of CO as a feedstock in many important industrial processes, such as methanol synthesis and the Fischer–Tropsch process which produces synthetic liquid fuels. Most extensively researched RWGS catalysts are based on Cu, Pt or Fe.¹ Metal nanoparticle-support interface is the reactive perimeter (active site)², and the reaction proceeds via the formate, carbonate or redox mechanisms, which are still debated. On reducible supports such as TiO₂ and CeO₂, the redox mechanism is often dominant and CO₂ dissociation is the rate determining step.³ Strong CO binding to metallic sites (Pt and Ni) overpopulates them, making them inaccessible for H₂ activation,⁴ which results in absence of low temperature activity (below 200 °C). Direct catalytic activation of CO₂ over copper is energetically very demanding and is greatly accelerated in substantial H₂ excess.⁵ Thus, innovative pathways for accelerating RWGS rate under H₂ lean conditions and at low temperatures (below 200 °C) are highly desired.

Photo-thermal catalysis can influence reaction rates via modification of binding strength of reactants, intermediates and products, as well as direct oxidation and reduction half reactions with participation of hot carriers such as electrons and holes.⁶ Yang et al.⁷ report that the RWGS activity of 5 %Cu/CeO₂ catalyst upon visible light illumination increased by 30 % at 250°C. A combination of *In-situ* DRIFTS, EPR, and XPS characterization demonstrate that under visible light irradiation, the localized surface plasmon resonance (LSPR) produced by Cu nanoparticles stimulates hot electrons transfer to ceria, causing destabilization and desorption of bidentate formate and linear-CO intermediate species. Moreover, the spillover of H₂ from Cu to CeO₂ surface is also affected by light due to the observed regeneration of oxygen vacancies on the CeO₂ surface, which positively influences the CO yield.

In this work we investigate the effects of visible light on the photo-thermal CO₂ reduction to CO using visible light and a commercial Cu-ZnO-Al₂O₃ catalyst. Copper is the main component of the investigated catalyst and is a plasmonic metal with a strong localized surface plasmon resonance around 600 nm, and ZnO is a semiconductor with a bandgap of about 3.2 eV. This makes the Cu-ZnO-Al₂O₃ material a promising candidate also for photo-thermal catalytic reactions.

EXPERIMENTAL

A commercial Cu-ZnO-Al₂O₃ catalyst (HiFuel R120™) with a nominal composition of 45% CuO, 25% ZnO, 15% Al₂O₃ and graphite binder, was purchased from Alfa Aesar. This catalyst is used for methanol steam reforming. Due to the principle of microkinetic reversibility, the same catalyst can be used also for methanol synthesis at high pressures, or CO formation via reverse water gas shift reaction at low pressures. During this research, we performed N₂ physisorption measurements, XRD analysis, UV-Vis diffuse reflectance spectroscopy of the catalysts before and after activation, *in-situ* DRIFT-MS and visualization by SEM microscopy. Catalytic and photocatalytic experimentation was done in a flow through Harrick reaction chamber with visible light illumination (Schott, model KL2500 or Fianium SuperK supercontinuum laser). For catalytic experiments, 22 mg of powdered sample was first activated in 5% H₂/N₂ flow at 320°C for 30 minutes, and experiments were performed between 200 and 320°C using a flowrate of 30 ml/min containing 50% H₂ and 50% CO₂.

RESULTS AND DISCUSSION

XRD analysis of HiFuel R120 catalyst before and after activation in diluted H₂ flow confirmed transformation of CuO into nanosized metallic copper crystals (18 nm), Figure 1a. In addition, ZnO (11 nm) and graphite binder were identified, which is consistent with nominal catalyst composition.

The N₂ sorption isotherms are typical Type III according to IUPAC classification, and are characteristic of mesoporous materials containing interparticle porosity, Figure 1b. The calculated BET specific area was 67 m²/g and the total pore volume 0.25 cm³/g.

The UV-Vis DR spectra of the sample before and after activation showed notable differences (Figure 1c), mainly in the formation of two absorption peaks centered at 559 and 488 nm, which could be assigned to localized surface plasmon resonance of metallic copper (Cu LSPR)⁸, and inter and intra band electron transitions in copper, respectively.⁹ The broad band around 800 nm which appeared only in the activated sample can be assigned to d-d transitions of Cu²⁺ ions in a distorted octahedral symmetry, which are probably related to formation of CuAlO₄ spinel phase.¹⁰

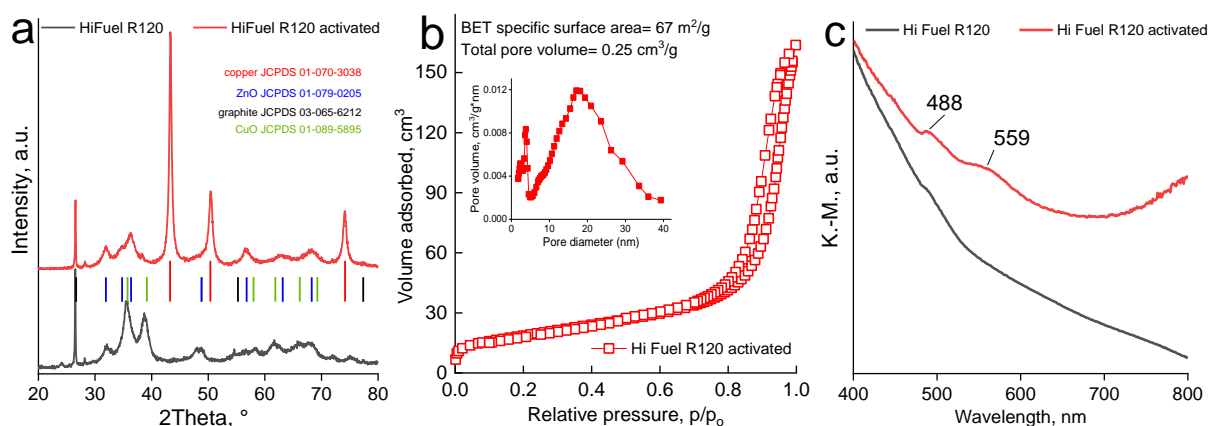


Figure 1. a) X-ray diffraction patterns, b) N₂ sorption isotherm with inset showing pore size distribution and c) UV-Vis DR spectra of the catalyst before and after activation.

UV-Vis DR spectra of the HiFuel R120 catalyst before and after activation.

When the RWGS reaction was driven only by thermal energy (thermo-catalytic mode), only CO was formed and no other carbon containing side products (like methane or methanol). The CO formation rate increased exponentially with increasing temperature (as expected), and the Arrhenius analysis revealed the apparent activation energy of 83 kJ/mol (Figure 2a).

The photo-thermal experiment was performed by constantly illuminating the catalyst with visible light ($\lambda = 400\text{-}700\text{ nm}$, Irradiance = 770 mW/cm^2) and changing the power output of the electric heater to control the catalyst temperature. The CO formation rate was up to 6-times higher in the photo-thermal experiment compared to thermocatalytic one at a catalyst temperature of $206\text{ }^\circ\text{C}$. The operating temperature range was extended downwards substantially: CO was already formed at $143\text{ }^\circ\text{C}$, whereas in the thermally driven reaction, no activity was observed below $206\text{ }^\circ\text{C}$. Furthermore, the apparent activation energy was lowered to 50 kJ/mol, Figure 2a. This suggests a notable change of the RWGS reaction mechanism under thermally driven and photo-thermal conditions, respectfully.

To further analyze the alterations of the reaction mechanism, kinetic analysis was performed. In dark, the CO_2 and H_2 reaction orders were 0.89 and 0.71. However, under photo-thermal conditions, the CO_2 reaction order remained mostly unchanged at 0.81, whereas H_2 order decreased to -2.6. A negative reaction order suggests CO_2 and H_2 are competing for the same active sites under illumination. The active sites are strongly overcrowded by chemisorbed hydrogen which hampers CO_2 adsorption and dissociation.

Different wavelength ranges (400-460 nm, 600-660 nm and 790-850 nm) were tested for their ability to accelerate CO rate, Figure 2b. The three ranges roughly correspond to excitation of inter- and intra-band transitions of metallic copper, Cu LSPR and Cu^{+2} d-d transitions (Figure 1c). For all utilized wavelength ranges, different extent of CO rate acceleration was observed, and shortest wavelengths (400-460 nm) proved most efficient to drive the reaction. The CO rate under repeated reaction conditions did not drop, revealing the tested catalyst is stable under applied reaction conditions.

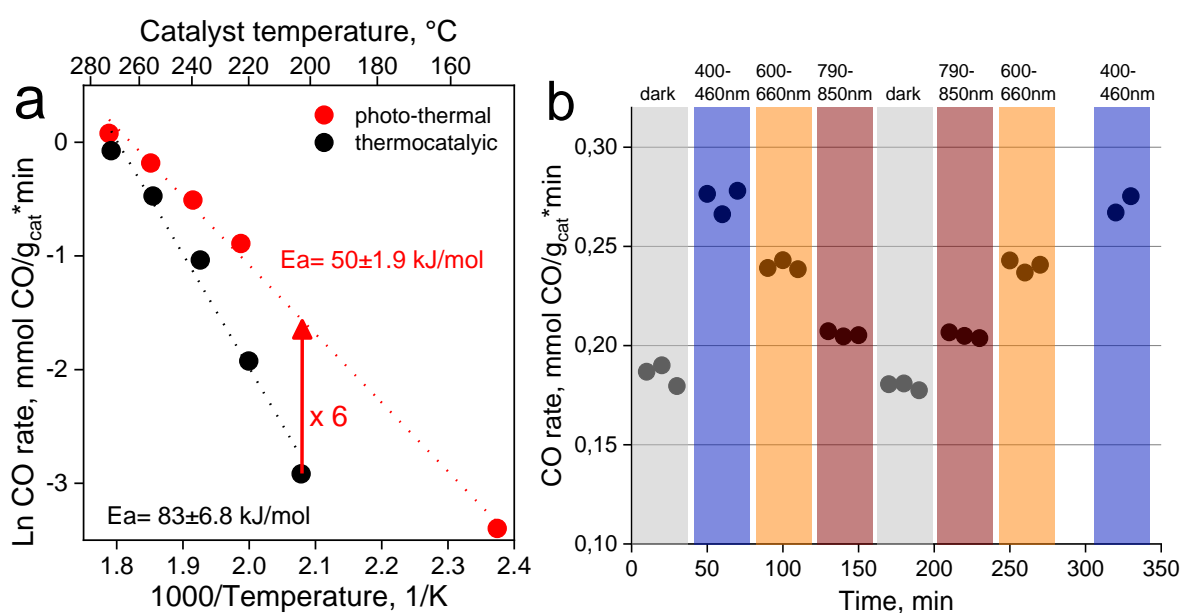


Figure 2. a) Arrhenius plots for CO formation and corresponding apparent activation barriers for the thermally

driven and photo-thermal RWGS reaction, b) CO rate in thermally driven and photo-thermal conditions using different wavelength ranges and irradiance of 7.1 W/cm². The catalyst temperature was maintained constant at 230°C.

CONCLUSION

We confirmed that composite catalysts comprised of plasmonic metal (Cu) and semiconductor (ZnO), which act as light harvesting and catalytic components enable both thermally driven and photo-thermal CO₂ reduction reaction. When a combination of visible light and thermal energy is used to sustain the RWGS reaction, the reaction rate is notably higher, and the activation barrier is decreased. Apparently light enables the catalytic turnover to proceed in an energetically less demanding pathway with higher frequency.

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