# Investigating metal-support interactions on the reverse water gas shift reaction in nonthermal plasma chemistry

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**Abstract:** The influence of metal-support interactions between group 13 oxides (γ-$Al_2O_3$, c-$In_2O_3$, and β-$Ga_2O_3$) and Cu nanoparticles were studied in the reaction between $CO_2$ and $H_2$, known as the reverse water gas shift. In a packed-bed coaxial dielectric barrier discharge reactor, Cu/c-$In_2O_3$ reactivity was distinct, achieving 25% $CO_2$ conversions over eight hours. We hypothesize surface oxygen vacancies facilitate $CO_2$ absorption, increasing activity.

## 1. Introduction

Plasma-driven catalysis of Cu nanoparticle catalysts on group 13 oxides (γ-$Al_2O_3$, c-$In_2O_3$, and β-$Ga_2O_3$) were studied. Metal-support interactions are critical factor that influences catalytic performance, yet many unknowns remain about how these effects are impacted in plasma-catalyst environments.[1] We studied the reverse water gas shift reaction (rWGS; $CO_2 + H_2 \rightarrow CO + H_2O$) given its significance in carbon mitigation and the role of catalysts in selectively producing hydrocarbons and oxygenates from the reaction mixture.

Cu was selected as the catalytically active metal because it is the industrial standard for $CO_2$ hydrogenation reactions.[2] Group 13 oxides present a way to probe support effects because of the variability in reducibility, metal-support interaction, as well as being widely studied for this reaction.[2,3] The interfacial sites between the metal and metal oxide are critical for key reaction steps, such as $CO_2$ absorption.[3] This study was designed to understand the oxide support effects on conversion and selectivity of the rWGS reaction.

## 2. Methods

A coaxial dielectric barrier discharge reactor was packed with 500 mg of catalyst. 5 sccm of $CO_2$ and 15 sccm of $H_2$ were flowed through the catalyst bed. Plasma was generated surrounding the catalyst bed using 15kV peak-to-peak alternating current pulsed at 500Hz (PlasmaLeap Technologies Leap100). Product gases were monitored by gas chromatography over eight hours to assess product yield, $CO_2$ conversion, and catalyst stability. The catalysts studied were 4% weight-loading of Cu nanoparticles supported on γ-$Al_2O_3$, c-$In_2O_3$, and β-$Ga_2O_3$, synthesized via wet impregnation. The bare oxides were also assessed. Catalysts are characterized by SEM, EDS, XPS, pXRD, and $N_2$ physisorption.

## 3. Results and Discussion

Figure 1 shows the $CO_2$ conversion as a function of time on stream. 10% $CO_2$ conversion was observed in the absence of catalyst (empty reactor), confirming plasma-driven excitation of $CO_2$ is sufficient to dissociate the $CO_2$ double bond. CO selectivity was greater than 99%, but methane, ethane, and methanol were also observed. The presence of catalyst enhances the production of CO from $CO_2$ in all cases. Cu/c-$In_2O_3$ led to the highest $CO_2$ conversion; we hypothesize this due to the presence of oxygen vacancies in the oxide lattice stabilized by the Cu nanoparticles.[3] c-$In_2O_3$ underwent the most significant increase in activity with the addition of Cu nanoparticles. Bare γ-$Al_2O_3$ exhibited the highest selectivity for methanol and ethane formation, while Cu/β-$Ga_2O_3$ was the most selective towards methane. No conversion was observed over any catalyst in the absence of plasma at room temperature.

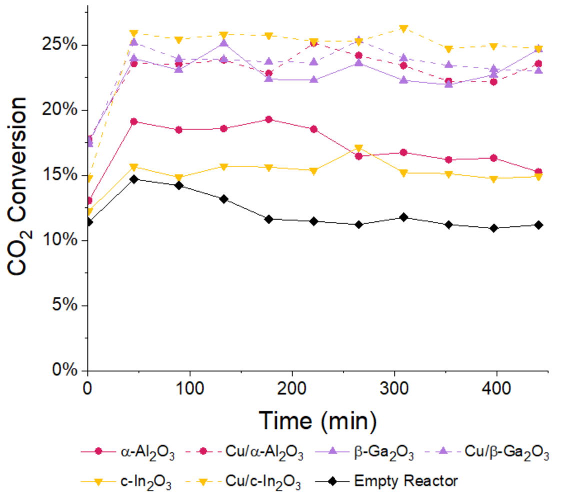

**Fig. 1**. $CO_2$ conversion as a function of time.

## 4. Conclusion

$CO_2$ conversions of over 25% were achieved by Cu nanoparticles supported on c-$In_2O_3$ due to stabilized oxygen vacancies. While the plasma excitation of the gas phase $CO_2$ contributes to conversion, enhancement with the incorporation of a catalyst indicates a synergistic relationship between plasma and catalyst.

## References

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