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# Synergistic promotion of vibrant H radicals and targeted Cu/MgAlO interface for $CO_2$ hydrogenation by non-thermal plasma

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## 1. Introduction

As the sustaining global warming, researchers now pay more attention to the conversion of $CO_2$ and the $CO_2$ hydrogenation is a promising method to dispose it with a source to provide valve-added chemicals[1]. Of these, $CH_3OH$ is especially interesting, as it is a precursor for formaldehyde, dimethyl ether, gasoline, and olefins.

In low-temperature plasmas, high-energy electrons (with an average electron temperature of 1-10 eV) collide with stable molecules and activate them, while the bulk gas temperature remains low [2]. Despite the growing research activity in plasma-enhanced catalysis, we still do not fully understand the relationship between the catalyst properties and overall reaction performance. In this work, we studied the effect of metallic Cu sites, as well as the MgO and $Al_2O_3$ supports on the conversion and selectivity of $CH_3OH$ during plasma-enabled $CO_2$ hydrogenation process. Meanwhile, to differentiate the catalytic roles of Cu and the MgAlO support, we designed an *in-situ* plasma-coupled Fourier transform infrared (FTIR) chamber to detect surface adsorbed species, thereby establishing a correlation between surface species and $CH_3OH$ selectivity. To further elucidate the reaction mechanisms, zero-dimensional simulations and atomic-level DFT calculations were performed to explore the reaction rate, radical density of the gaseous radicals and the surface reaction barriers at the Cu/MgAlO interface.

## 2. Experimental Setup

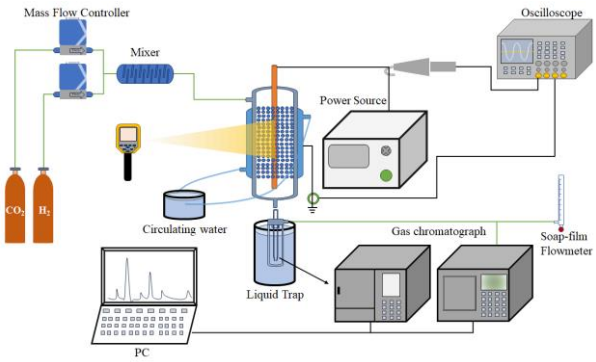


**Figure 1.** Schematic diagram of the experimental setup.

In this work, the nanosecond pulsed power source and coaxial dielectric barrier discharge (DBD) reactor were used for $CO_2$ hydrogenation. The whole experimental set-up (shown in Figure 1) and the activity evaluation process including reactant conversion rate, product selectivity, C/H balance can be seen in our previous studies [3].

## 3. Results and Discussion

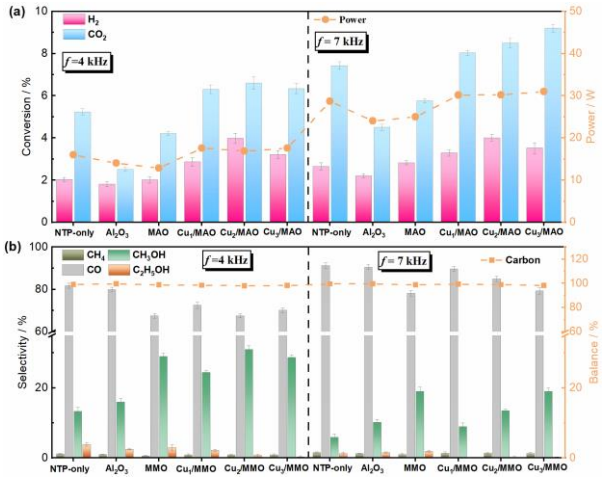


**Figure 2.** Conversion characteristics for variable Cu-based catalysts using different discharge frequencies.

Contrary to the commonly considered inactive phase of oxide support, hydrogenation tests in Figure 2 revealed the independent relationships between Cu center and MgAlO support. We found that the MgAlO oxide support contributed to $CH_3OH$ selectivity while the existence of Cu was essential to promote $CO_2$ conversion. Furthermore, the co-feeding $H_2$ and $H_2O$ could provide sufficient vibrant H radicals via electron impaction thus synergistically promoting $CH_3OH$ selectivity (51.3%) and energy efficiency (166.2 $mmol \cdot kWh^{-1} \cdot g^{-1}$) over Cu/MgAlO interface. Notably, the *in-situ* plasma FTIR demonstrated that the enhanced $CH_3OH$ selectivity is directly proportional to surface formate concentration, while it showed little relation with the active phase size. Combined with systemic microstructure characterizations of Cu/MgAlO, we utilized DFT and zero-dimension calculations to thoroughly explore the synergistic effect over the Cu/MAO interface facilitated by active H radicals *via* plasma-assisted formate and CO hydrogenation routes.

## References

[1] *Chemical Society Review, 49, 1385 (2020).*
[2] *Appl. Catal. B-Environ., 318, 121830 (2022).*
[3] *Plasma Process Polym. 21, 2300069 (2024).*