

## Coupling nanosecond pulsed plasma with nanocatalysts for efficient CO<sub>2</sub> conversion into liquid Chemicals

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Nowadays, there is growing interest into various strategies to convert CO<sub>2</sub> into value-added chemicals. This is particularly challenging as CO<sub>2</sub> is a molecule with high thermodynamic stability. The integration of plasma with nanocatalysts is a promising way to improve the selectivity of liquid oxygenates for CO<sub>2</sub> conversion due to the strong synergy effect<sup>[1]</sup>. In general, plasma catalysis has the potential to bypass slow reaction steps in thermal catalysis through reactive gas phase processes in the plasma and to improve the selectivity toward desired products compared to plasma alone due to the presence of a catalyst. In nonthermal plasma, 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<sup>[2]</sup>. Despite the growing research activity in plasma-enhanced catalysis, we still do not fully understand the relationship between the catalyst properties and overall reaction performances<sup>[3]</sup>.

In this work, we studied the effect of plasma treated supported Co-based catalysts on the CO<sub>2</sub> conversion and selectivity of CH<sub>3</sub>OH during the CO<sub>2</sub>+H<sub>2</sub>+H<sub>2</sub>O system. Meanwhile, we built a plasma-catalyst model to conduct zero-dimensional numerical simulations by ZDPlasKin. This reaction proceeded in a coaxial DBD reactor, in which the ground electrode consists of circulating water and is kept at 10 °C. Combined with the structure analysis of the catalysts, we observed that Co-based catalysts with the active CoO sites and abundant oxygen

vacancies can efficiently capture hydroxide radicals (OH) and promote to recombine with CH<sub>x</sub> radicals to form CH<sub>3</sub>OH, especially for the H<sub>2</sub>/Ar plasma treated CoO catalysts.

The results (Figure 1a) show that no obvious activity can be observed without plasma due to the thermal stability of CO<sub>2</sub>. Notably, integrating plasma with treated CoO catalyst can easily drive the CO<sub>2</sub> conversion in the mixture system (CO<sub>2</sub>+H<sub>2</sub>+H<sub>2</sub>O). As for the products (Figure 1b), we can see that the selectivity of CH<sub>3</sub>OH was only 16.2% under plasma-only mode. When H<sub>2</sub>O was added, the selectivity of CH<sub>3</sub>OH increased to 20.7%, indicating the promotion effect of H<sub>2</sub>O on CH<sub>3</sub>OH synthesis through providing more OH radicals. Moreover, packing CoO catalyst clearly increased the selectivity of CH<sub>3</sub>OH from 17.4% to 28.2%, demonstrating that surface reaction greatly contributed to the CH<sub>3</sub>OH formation. Impressively, the H<sub>2</sub>/Ar-CoO further maximized the selectivity of CH<sub>3</sub>OH to 39.6%, implying the importance of the pre-treatment of CoO catalyst for the selective synthesis of CH<sub>3</sub>OH.

### References

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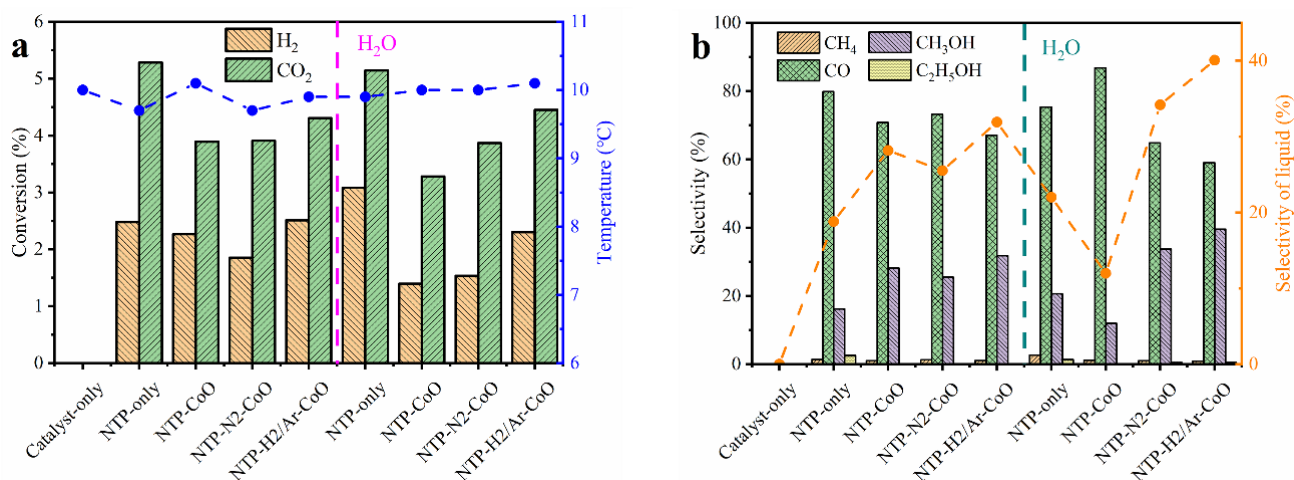


Figure 1. (a) The conversion rates and (b) the selectivity of CH<sub>4</sub>, CO, CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH over plasma-treated CoO catalyst in plasma-involved CO<sub>2</sub>+H<sub>2</sub>+H<sub>2</sub>O system.