

Plasma-catalytic CO₂ hydrogenation over a Pd/ZnO catalyst: *In situ* probing of gas-phase and surface reactions

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Abstract: Plasma-catalytic CO₂ hydrogenation is a complex process involving both the gas-phase and plasma-assisted surface reactions. Herein, we investigated CO₂ hydrogenation over Pd/ZnO and ZnO in a coaxial dielectric barrier discharge (DBD) plasma reactor at ambient pressure. Compared to the CO₂ hydrogenation using plasma only or plasma+ZnO, packing with Pd/ZnO significantly enhanced the conversion of CO₂ (36.7%) and CO yield (35.5 %). *In situ* FTIR coupled with MS were applied to reveal the mechanism thoroughly.

Keywords: Non-thermal plasma, Plasma catalysis, CO₂ hydrogenation.

1. Introduction

CO₂ conversion is considered an important strategy to reduce CO₂ emissions while producing valuable fuels and chemicals for energy storage. However, CO₂ is a very stable chemical, thus the conversion of CO₂ often requires high temperature and/or high pressure with the presence of a catalyst. Significant efforts have been devoted to exploring and investigating different catalytic routes for CO₂ valorization, such as CO₂ hydrogenation, CO₂ decomposition and dry reforming of methane (DRM) with CO₂. Conversion of CO₂ with H₂ to CO, also called the reverse water gas shift (RWGS) reaction, has received increasing interest recently, especially in conjunction with the Fischer-Tropsch process in the interest of producing hydrocarbon fuels. However, RWGS is an energy-intensive process as this reaction is endothermic and thus is thermodynamically favorable only at higher temperatures.

Non-thermal plasma (NTP) is an emerging technology for CO₂ valorization under mild conditions [1-3]. Energetic electrons generated by NTP can react with reactants (e.g., CO₂) and generate a cascade of active and energetic species such as ions, free radicals, excited molecules and atoms, which might not exist in thermal or catalytic processes. The unique non-equilibrium character of NTP enables the progression of thermodynamically unfavorable reactions (e.g., RWGS) in ambient conditions. In addition, NTP processes are instantaneous allowing them to be switched on as needed, providing tremendous flexibility for integration with renewable energy sources such as wind turbines and solar panels, especially with the use of intermittent renewables for decentralized chemical energy storage. In addition, coupling NTP with catalysis (plasma catalysis), also offers the notable prospect of generating a synergistic effect arising from the physicochemical interactions between the NTP and catalyst [4], offering an effective way for the selective production of chemicals and fuels from CO₂ with enhanced conversion and energy efficiency. However, plasma-catalytic chemical reactions (e.g., CO₂ hydrogenation) are a complex chemical process, with a combination of gas-phase plasma reactions and plasma-assisted surface reactions. The exact reaction pathways in the plasma-assisted catalytic CO₂ hydrogenation (e.g., RWGS) have not been fully explored

and are still not clear, particularly the plasma-assisted reactions on surface of the catalyst, such as formation of intermediates on the catalyst, are largely unknown.

In this work, the plasma-catalytic hydrogenation of CO₂ over ZnO and Pd/ZnO was investigated using a typical tubular dielectric barrier discharge (DBD) NTP reactor. *In situ* plasma/FTIR combined with online MS and OES analysis was used to investigate the effect of ZnO and Pd/ZnO on the plasma-assisted gas-phase and surface reactions, particularly regarding generation of any intermediates on the catalyst surfaces in the plasma-catalytic CO₂ hydrogenation. Coupling these results with kinetic analysis, alternate reaction pathways for the plasma-enhanced catalytic CO₂ hydrogenation were proposed and discussed.

2. Materials and Methodology

Plasma-catalytic hydrogenation of CO₂ was conducted in a cylindrical DBD reactor. The detailed configuration and dimension of the reactor can be found in our previous work. The plasma reactor was connected to a high voltage alternating current power supply (Suman, CTP-2000K). A mixture of H₂ and CO₂ with an H₂/CO₂ ratio of 3:1 was used. The catalyst (0.5 g) was packed into the entire discharge gap and was reduced by H₂/Ar mixed gas (H₂/Ar = 1:9) at 400 °C for 4 h before the reaction. All the electrical signals were recorded using an oscilloscope (Tektronix DPO 3034). The plasma power was determined using the typical Lissajous figure approach.

3. Results and Discussion

The conversion of CO₂ and H₂ was 21.3% and 9.3%, respectively, in the plasma reaction with no packing. However, placing ZnO in the DBD did not enhance the conversion of CO₂ (20.2%) and H₂ (8.4%). In contrast, the combination of DBD with 2 wt.% Pd/ZnO notably improved the conversion of CO₂ and H₂ to 36.7% and 16.9%, respectively. This enhancement could be partially attributed to the formation of a ZnO_x overlayer with the presence of richer oxygen vacancies on the Pd/ZnO catalyst caused by the SMSI between ZnO and Pd, which is evidenced by the high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron

spectroscopy (XPS) analysis. The presence of the ZnO_x overlayer can effectively activate both H₂ and CO₂ for surface CO₂ hydrogenation. Despite this the conversion of both H₂ and CO₂ was less than 1% in the thermal catalytic CO₂ hydrogenation at 200 °C. In comparison to the plasma only system, the incorporation of plasma with ZnO or Pd/ZnO showed a similar CO selectivity (93.2-96.6%).

splitting of CO₂ to CO is believed to make major contributions to the conversion of CO₂, in both the gas phase and on the ZnO surface during the plasma-catalytic CO₂ hydrogenation over ZnO. The designed novel integrated DBD/FTIR gas cell reactor coupled with online MS and OES diagnostics offers a promising solution to develop greater comprehension of the reaction mechanisms and pathways for complicated plasma-catalytic chemical reactions, particularly plasma-assisted surface reactions.

4. References

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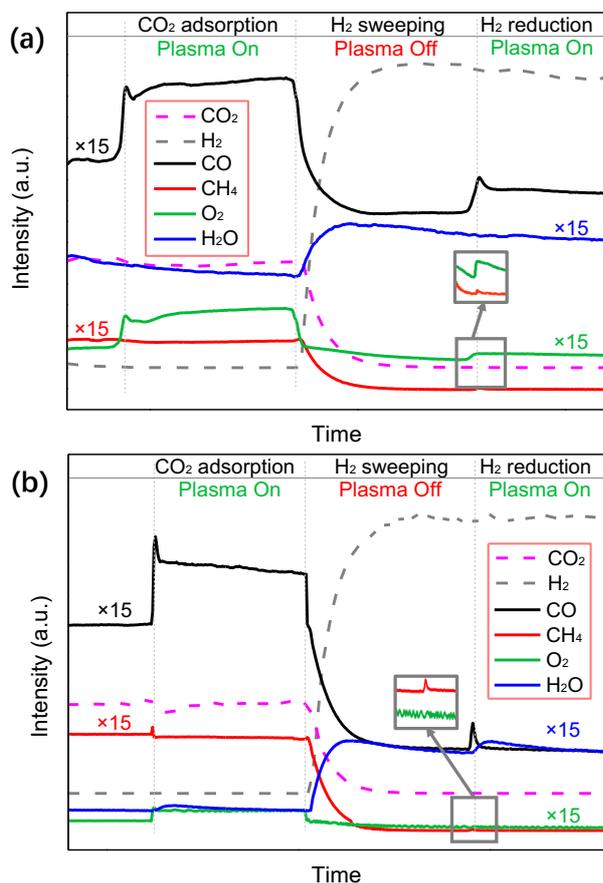


Fig. 1. Online MS analysis of plasma-catalytic CO₂ hydrogenation over (a) ZnO and (b) Pd/ZnO

In situ spectroscopy techniques including *in situ* FTIR, online MS (Fig. 1) and OES diagnostics combined with catalyst characterization and kinetic analysis were used to understand the role of Pd/ZnO in the plasma-catalytic CO₂ hydrogenation, particularly to develop a new understanding of the formation of intermediates on the catalyst surfaces. In the plasma-catalytic reaction using Pd/ZnO, the hydrogenation of adsorbed CO₂ on Pd/ZnO significantly contributes to the enhanced CO₂ conversion, which can be attributed to the formation of a ZnO_x overlay as a consequence of the SMSI between ZnO and Pd, and the presence of abundant H species (evidenced by plasma-assisted H₂-TPD analysis) on the Pd/ZnO surface due to H₂ activation by Pd NPs. However, without Pd loading, the hydrogenation of surface-adsorbed CO₂ on the ZnO surface was limited due to the absence of the SMSI and the lack of active H species formed on the ZnO surface. The