

Distribution of radicals in plasma catalysis for CO₂ methanation using an atmospheric pressure plasma jet

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Methanation is a process in which CO₂ is reduced with hydrogen to produce CH₄, aiming to contribute to carbon dioxide capture, utilization, and storage (CCUS). However, methanation is an exothermic reaction, and has challenges, including the intricate temperature control required during the process and catalyst degradation resulting from elevated temperatures.

Plasma catalysis is being considered as a solution to address this issue. It offers the advantage of lower activation energy compared to thermal catalysis by enabling non-thermal equilibrium plasma to act on the catalyst, and it exhibits a unique reaction [1]. Typically conducted in a packed-bed reactor, plasma catalysis involves packing the catalyst inside a dielectric tube, such as quartz glass. A mixture of CO₂ and H₂ gas is introduced into the tube, and plasma is applied to the catalyst. However, in the case of exothermic reactions, the catalyst temperature rises even in non-thermal equilibrium plasma, making it challenging to determine whether it is the effect of active species from the plasma or heat [2]. To investigate the interaction between radicals and catalyst surfaces, we generated H₂ and CO₂ plasma jets in dielectric barrier discharges (DBD) and irradiated Ru/TiO₂ to produce CH₄. The gases produced by plasma catalysis were analyzed by quadrupole mass spectrometer (QMS), and the catalyst surface conditions were analyzed by X-ray photoelectron spectroscopy (XPS). The distributions of H, OH, CO, and O radicals produced in this plasma experiment were measured by laser-induced fluorescence (LIF).

Figure 1 shows the QMS measurement results of gas compositions in both plasma catalysis and thermal catalysis. It reveals that CH₄ is produced in plasma catalysis when irradiated with Ar/H₂ plasma and Ar/CO₂ plasma, similar to the results observed in thermal catalysis. Upon comparing the specific energy input (SEI) for the same CH₄ yield, it is found that the reaction in plasma catalysis occurs at approximately a quarter of the energy in the thermal catalysis.

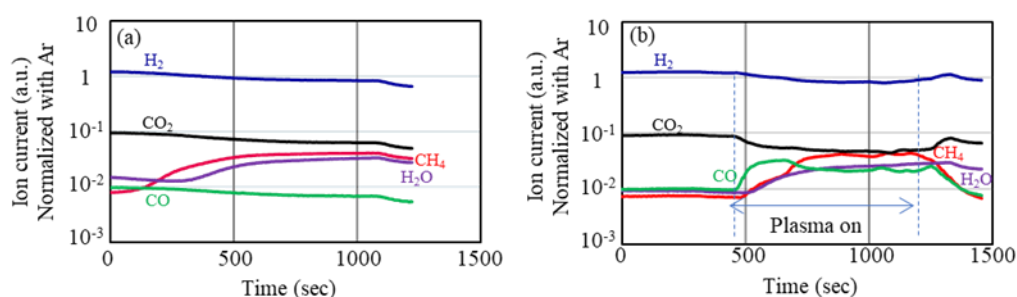


Fig.1 Gas analysis by QMS in catalytic reduction of CO₂ with H₂. (a) Thermal catalysis, (b) Plasma catalysis.

The XPS evaluation of the surface condition of Ru/TiO₂ is presented in Fig. 2. For reference, Fig. 2(a) shows the results without plasma, showing only the introduced gases, while Fig. 2(b) shows the outcomes of thermal catalysis. In both the cases, the gas introduction comprised 200 cm³/min of Ar, 20 cm³/min of CO₂, and 80 cm³/min of H₂, resulting in more RuO_x than Ru metal. No significant difference is observed between the results presented in Figs. 2(a) and (b). Figure 2(c) shows the effects of treatment with Ar/H₂ plasma, while Fig. 2(d) shows the results of the simultaneous irradiation of Ar/H₂ and

Ar/CO₂ plasmas. In both instances, RuO_x is reduced to Ru metal, but the simultaneous irradiation of Ar/H₂ and Ar/CO₂ plasmas leads to a more substantial reduction. The simultaneous generation and irradiation of Ar/H₂ and Ar/CO₂ plasmas suggest a possible oxidation of Ru metal by O radicals, derived from CO₂ decomposition. However, contrary to this expectation, the result indicates an accelerated reduction of RuO_x to Ru metal. To clarify this observation, we conducted a measurement of radicals in the plasma using LIF.

Fig. 2 XPS evaluation of Ru state on catalyst surface. (a) Only gas without power, (b) thermal catalysis, (c) Ar/H₂ plasma irradiation onto the catalyst, (d) simultaneous irradiations of Ar/H₂ and Ar/CO₂ plasmas onto the catalyst.

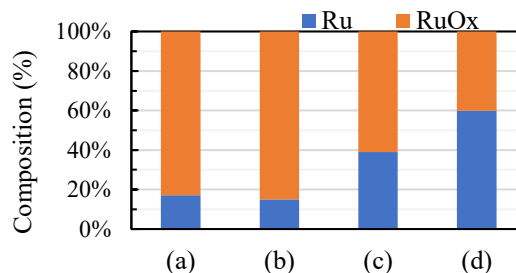


Figure 3 shows the results of two-photon absorption laser-induced fluorescence (TALIF) measurements of H radical density. The laser wavelength used for exciting H radicals in the plasma is 205 nm. The state of H radicals generated solely by Ar/H₂ plasma is depicted in Fig. 3(a), while those produced by Ar/H₂ and Ar/CO₂ plasma are presented in Fig. 3(b). Notably, the H radical density is higher when the catalyst was irradiated by the Ar/H₂ and Ar/CO₂ plasmas simultaneously, in comparison with the irradiation of the Ar/H₂ plasma alone. Additionally, in Fig. 3(b), the H radical density is higher in the Ar/CO₂ plasma side than the Ar/H₂ plasma side.

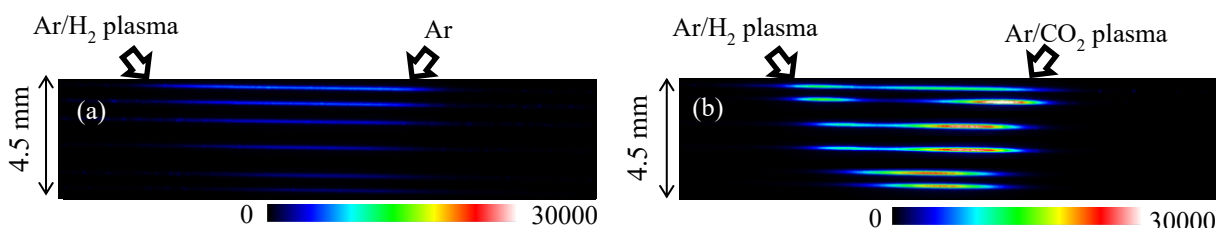


Fig. 3. H radical evaluation using TALIF. (a) Ar/H₂ plasma, (b) Ar/H₂ plasma and Ar/CO₂ plasma.

OH radical density in simultaneously generated Ar/H₂ and Ar/CO₂ plasmas were also measured using LIF, and the results are presented in Fig. 4. The laser wavelength for exciting OH radicals in the plasma is 262 nm. The OH radical density is higher in the Ar/CO₂ plasma side, aligning with the stronger intensity observed at the same position as the H radical in Fig. 3(b). These findings suggest that the O radical generated in the Ar/CO₂ plasma reacts with H₂ molecules to produce H radicals [3].

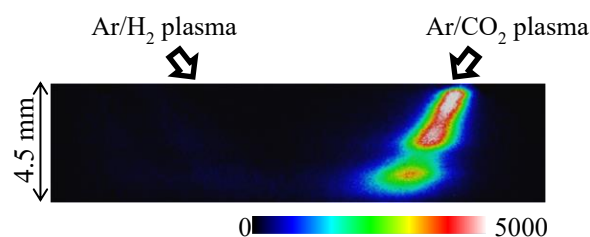


Fig. 4. OH radical evaluation using LIF with simultaneously generated Ar/H₂ plasma and Ar/CO₂ plasma.

In the plasmas examined in this study, H radicals were generated in the Ar/H₂ plasma, while O radicals were produced in the Ar/CO₂ plasma. Subsequently, the O radicals reacted with H₂ molecules, yielding H and OH radicals. These reactions, unique to plasma catalysis, are absent in thermal catalysis. The H radicals with a higher density, which is attributed to these reactions, reduce RuO_x to Ru metal on the catalyst surface, enhancing its activity. Consequently, methanation through plasma catalysis operates at lower energy levels than thermal catalysis.

References

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