9th Asia-Pacific Conference on Plasma Physics, 21-26 Sep, 2025 at Fukuoka

Sorption enhanced methanation with plasma catalysis using various types of zeolites

S. Toko[1], T. Okumura[2], K. Kamataki[2], K. Takenaka[1], K. Koga[2], M. Shiratani[2] and Y. Setsuhara[1]
[1] University of Osaka, Mihogaoka 11-1, Ibaraki, Osaka
[2] Kyushu University, Motooka 744, Nishi-ku, Fukuoka
e-mail: tokou.susumu.jwri@osaka-u.ac.jp

CO_2 methanation has attracted attention as a promising pathway for achieving a sustainable society. Traditionally, thermal catalysis is employed to accelerate the reaction; however, high temperatures are required, which can lead to catalyst deactivation. Recently, non-equilibrium plasma presented an alternative approach by enabling methanation at lower temperatures [1]. In plasma-assisted methanation, we have successfully suppressed the reverse reaction and enhanced CH_4 yield by adsorbing oxidation sources (H_2O, O, etc.) using molecular sieves (MS)[2]. This study examines the impact of various MSs placement—outside and inside the plasma—on methanation efficiency, what is called Post-Plasma Catalysis (PPC) and In-Plasma Catalysis (IPC).

Plasma was generated within a tube using a three-turn coil antenna, with a Cu mesh positioned at the tube's exit. H_2 and CO_2 were introduced from the top of the tube at a fixed CO_2/H_2 flow ratio of 1:6, while pressure was maintained at either 1 mTorr or 20 mTorr. To analyze gas composition, a quadrupole mass spectrometer was used, where mass number 15 corresponded to CH_4 partial pressure, and mass number 44 to CO_2 partial pressure. Two types of molecular sieves, MS 3A and MS 13X, were employed. The sieves were positioned 30 cm below the tube (PPC) and directly on the Cu mesh (IPC) to assess their influence.

Figure 1 shows the time dependence of CH_4 yield for PPC and IPC when using MS 3A or 13X. MS 3A is an adsorbent with a pore size of 3Å, capable of adsorbing molecules with an effective diameter under 3Å, such as H_2O. MS 13X has a pore size of 10Å, allowing it to adsorb molecules with an effective diameter under 10Å—such as CO_2, CO, and CH_4—which are important for methanation. When comparing the time dependence of PPC and IPC types, CH_4 yield decreases at around t = 300 s in both MS 3A and MS 13X for IPC systems. Additionally, when using MS 3A, PPC systems maintain a higher CH_4 yield throughout all time periods. However, when using MS 13X, the IPC system shows a higher CH_4 yield before the decline.

The decrease in CH_4 yield at a certain time suggests adsorption capacity reached its limit. There are two possible reasons for the earlier adsorption limit in IPC; 1. heating of the MS reduced its adsorption capacity, 2. many radicals were adsorbed.

Generally, higher temperatures reduce MS adsorption capacity. In IPC systems, heat generated from plasma cannot be ignored, leading to reduced adsorption capacity and accelerated deactivation. Additionally, IPC systems likely adsorbed a larger quantity of radicals and excited species, further contributing to deactivation.

This analysis also explains differences in effective MS placement for MS 3A and 13X. For MS 3A, which primarily improves CH_4 yield by adsorbing oxidizing agents, PPC systems are effective as they prevent MS heating. On the other hand, MS 13X contributes to CH_4 formation through both oxidizing agent adsorption and interactions with excited CO_2, CO species, or H radicals colliding and adsorbing into pores, making IPC systems more effective.

References

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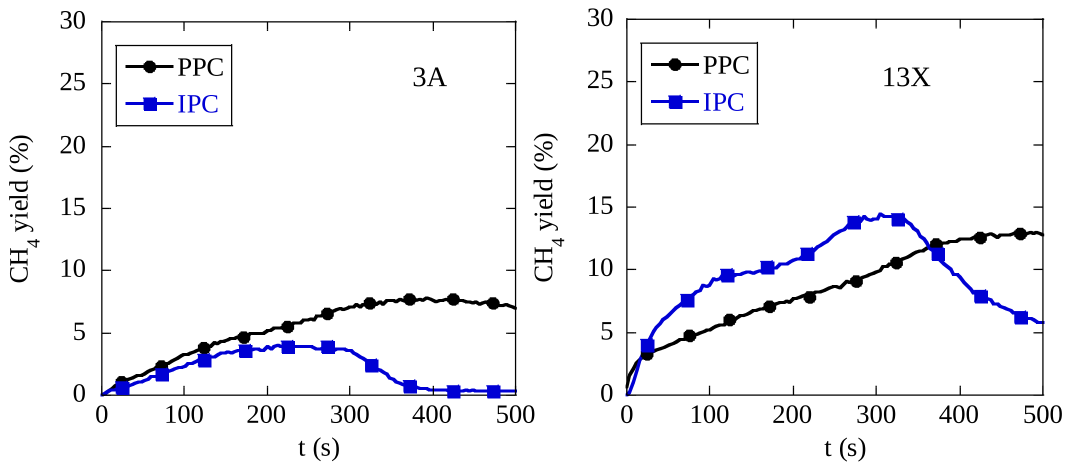

Figure 1. Comparison of the time dependence of CH_4 yields in PPC and IPC types with MS 3A (left) and 13X (right)