Online LTP Seminar
Lecture 10
September 15, 2020

Plasma enabled heterogeneous catalysis for greenhouse gas conversion: kinetic modeling

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Abstract - A mode-selective control of the surface reaction is expected to be a promising approach in the heterogeneous catalysis. Nonthermal plasma is a vital solution for the generation of vibrationally excited molecules, thereby enhancing mode-selective surface chemistry. Especially, plasma-enabled promotion of heterogeneous catalysis for CH_4 conversion attracts keen attention because the strong C-H bond breaking is possible via vibrational excitation of CH_4 at low temperature. Similarly, vibrational excitation of CO_2 possesses unique reactivity in heterogeneous catalysts [1-2].

This presentation focus on a rigorous determination of kinetic parameters of CH_4 and CO_2 reforming to elucidate the drastic reaction promotion mechanism enabled by plasma-catalyst interaction. Lanthanum-modified Ni/Al_2O_3 catalyst was combined with dielectric barrier discharge (DBD) at 5 kPa and 400-700 degC without dilution gas. Determination of surface coverage of plasma-excited species is discussed based on Langmuir-Hinshelwood mechanism. The Arrhenius plot for forward CH_4 rate constant revealed that 12 kHz DBD hybrid reaction is characterized as mixed catalysis where plasma and thermal catalysis are not decoupled. The apparent activation energy was influenced only slightly by the specific energy input (SEI, eV/molecules) and gaseous hourly space velocity (GHSV, h^{-1}), because the electrical properties of *streamer swarm* are not influenced to a large extent by either SEI or GHSV at fixed frequency. In contrast, 100 kHz DBD yielded significant improvement of CH_4 and CO_2 conversion via vibrational excitation. Activation energy decreased from 91 kJ/mol to 44.7 kJ/mol. The reason "why activation energy is halved", "what would be the minimum activation energy achieved" would be answered by the state-specific gas-surface reactivity of vibrationally excited CH_4 on Ni surfaces in the molecular beam study. The mechanism discussed here would be applied to other plasma catalysis system such as N_2 to NH_3, CO_2 hydrogenation, and CH_4 coupling to higher hydrocarbons.

1. Annemie Bogaerts, Xin Tu, J Christopher Whitehead, Gabriele Centi, Leon Lefferts, Olivier Guaitella, Federico Azzolina-Jury, Hyun-Ha Kim, Anthony B Murphy, William F Schneider, Tomohiro Nozaki, Jason C Hicks, Antoine Rousseau, Frederic Thevenet, Ahmed Khacef and Maria Carreon, The 2020 Plasma Catalysis Roadmap, *Journal of Physics D: Applied Physics*, 53, 443001(51pp), 2020.
2. Zunrong Sheng, Yoshiki Watanabe, Hyun-Ha Kim, Shuiliang Yao, Tomohiro Nozaki: Plasma-enabled mode-selective activation of CH_4 for dry reforming: First touch on the kinetic analysis, *Chemical Engineering Journal*, 399, 125751(14pp), 2020.

Brief Bio:

Tomohiro Nozaki received B.E. and M.E. degrees from Toyohashi University of Technology, Japan, both in Energy Engineering, in 1993 and 1995. He started his carrier at Ishikawajima-Harima Heavy Industries. Co. Ltd. (currently IHI) ('95–'96), where he engaged in the pulverized coal combustion and the environmental protection technology development. He became a faculty of Gifu University in Mechanical Engineering ('96–'99) and an Assistant Professor of Tokyo Institute of Technology in the Department of Mechanical Engineering ('99). He directed his research to the atmospheric pressure plasma chemistry and received Ph.D. from Tokyo Tech in 2003. After his postdoctoral work at the University of Minnesota ('03–'04), he received full professorship from Tokyo Institute of Technology in 2012. He pioneered various innovative plasma processing technology based on atmospheric pressure plasmas and is exploring new technology in the fields of Plasma Catalysis, Electron-driven chemistry, Natural gas conversion, and Silicon nanoparticles synthesis and photovoltaic application. He is the author of more than 150 publications including several book chapters (international and domestic). He is currently a Board of Director of International Plasma Chemistry Society, Editorial Board of Plasma Chemistry and Plasma Processing (Springer), International Advisory Board of Plasma Processes and Polymers (Wiley).