

Approaching the reaction equilibrium through a non-equilibrium approach: Plasma catalytic synergy for low-temperature CO₂ Methanation

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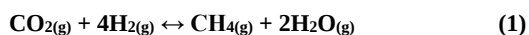
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Abstract: The thermodynamic and kinetic limitations often restrict the feasibility and scalability of conventional catalytic processes for CO₂ methanation at the industrial level. Due to the non-equilibrium nature of non-thermal plasma, reaction barriers can be overcome that proves this approach viable for this conversion even at low temperatures. This work reports the modified chemistry in plasma-catalytic interaction over Nickel based catalyst. It also depicts the role of plasma and catalyst and the synergy between them. It is found that the conversion of CO₂ under plasma was approximately 60% at 150 °C that corresponds to the higher temperatures in thermal catalysis. The application of non-equilibrium plasma provides an alternative pathway that leads to low-temperature CO₂ transformations with acceptable conversion, selectivity, stability and controllability.

Keywords: CO₂ breakdown, low-temperature conversion, solid phase, synergistic effects

1. Introduction

Carbon emissions now become a potential threat to the environment as Green House Gas (GHG) contributing in global warming and scientific world is focusing to minimise its effects by capturing, sequestration and recycling of CO₂. In 2014, Carbon emissions were estimated as 9855 million metric tons which were highest ever and 0.8% more than in 2013 and expected a 2-3% rise in next five years [1] [2]. In the present scenario, the utilisation/conversion of carbon oxides as raw material into fuels is the most feasible solution for sustainable development in the perspective of energy and environment. In this context, many efforts have been made to convert carbon oxides to valuable chemicals like methane or other fuels since a few decades. Sabatier's reaction is the fundamental route for the reduction of CO₂.



The thermodynamically stable molecule such as CO₂ and kinetically limited reaction for the carbon dioxide splitting at low temperature and atmospheric pressure are major constraints. The role of an external agent (electric field) in the presence of transition metal-based active sites and how it affects the activity, reactivity and selectivity during the process is the focus of this study. Under the non-thermal and non-equilibrium plasma, the conversion mechanisms, surface behaviours, transport phenomena and rate determining steps can play an important role for the low energy conversions. Thermodynamic and kinetic constraints are major limitations in this process and make this conversion highly energy intensive. Plasma-assisted

catalysis may be a key alternate solution to this problem. Plasma-catalytic methanation is a novel technique in which Carbon dioxide can be reacted with hydrogen in discharge at atmospheric pressure. Dielectric barrier discharge (DBD), microwave (MW), corona, pulse etc. discharges have been shown as effective systems for chemical conversion such as CO₂ splitting/dissociations [3]–[5], CO₂ hydrogenation[6]–[9], methane reforming[10], [11], VOC destruction [12], [13], methane to oxygenates [14], [15]. Plasma technology combined with catalysis has more focused for low temperature and atmospheric conversions in replacement of thermal systems. The most recent advancements in this area lead to its full potential, however fundamental issues, phenomenological understanding, technological and scientific challenges must be addressed to get effective, efficient but economical conversions. This technology can be way forward to next-generation targets from “Zero Emissions” to “Negative Emissions”.

2. Approach

In this work, the CO₂ hydrogenation reaction was systematically investigated under thermal and non-thermal, non-equilibrium dielectric barrier discharge (DBD) for both catalytic and non-catalytic configurations. The packed bed DBD reactor was designed, and setup was built to perform these experimentations with efficacy. Nickel, sometimes, considered as a highly efficient and cost-effective metal under the desired reaction conditions. Nickel-based catalysts were synthesized with different metal loadings (wt%) supported on commercial alumina. The packed bed configuration was used for performance

tests constituted by the inert glass beads for uniform catalyst and homogeneous discharge distributions. The following approaches were adopted to analyse the performance: 1) Plasma discharge only; 2) Plasma discharge in inert beads; 3) plasma discharge in 0% metal loading bed, and 5) plasma discharge in x % metal loading bed. The reactants and products were analysed through an in-line gas chromatograph (TCD and FID). Thermal tests were also performed with similar approaches to develop a basis for comparison.

In addition to this, pre- and post-activity catalyst characterisations were conducted extensively via hydrogen temperature programmed reduction (H_2 -TPR), Brunauer-Emmett-Teller (BET), Inductively coupled plasma optical emission spectroscopy (ICP-OES), (X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), High resolution transmission electron microscopy (HR-TEM) to access the impact of plasma on nickel nanoparticles. In-situ optical emission spectroscopy (OES) was also used to capture the real-time reaction footprints in catalyst bed under plasma discharge.

3. Results & Discussion:

A series of experiments were performed to investigate the behaviour of the reactant species and nickel-based catalyst under plasma and their mutual interactions. For the 10 % nickel supported by alumina, 60% carbon dioxide conversion was achieved with 99% selectivity towards methane at 150 °C. Thermally, only 2-3 % carbon dioxide conversion was reported on the same conditions as shown in Figure 1.

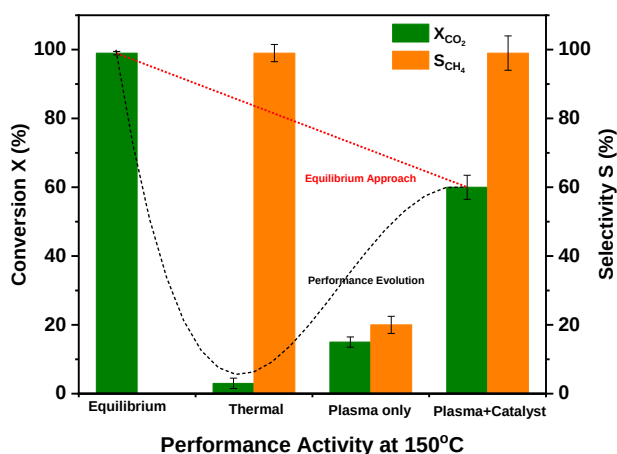


Figure1: Reaction performance of different operating modes (thermal, plasma discharge only, plasma discharge + catalyst) compared with equilibrium conversion at 150 °C. Red and black dotted lines demonstrate the low-temperature system approach towards equilibrium and the system-based performance evolution respectively

Also, the characterizations show the catalyst is very stability under plasma discharge and nickel being an active performer in discharge to generate methane in bulk (higher selectivity) whereas plasma is the playing its role as driving force through reactants activation into number of species that are easy to transform into methane after interaction with nickel surface at low temperature.

Overall, these results indicate the synergism between plasma discharge, reactant species (CO_2 and H_2) and the catalyst material (Ni), where each contributes a different way through unconventional mechanisms.

4. Significance

This work demonstrates the role of plasma in catalytic methanation as a driving force instead of high temperature. The novelty lies in the development of scientific understanding of the activation behaviours in gas (CO_2 and H_2) as well as solid (catalyst) phase under discharge and their synergistic effects for selective transformation to methane.

5. References

- [1] T. A. Boden, G. Marland, and R. J. Andres, "Global, Regional, and National Fossil-Fuel CO_2 Emissions," *Carbon Dioxide Inf. Anal. Center, Oak Ridge Natl. Lab. U.S. Dep. Energy, Oak Ridge, Tenn., U.S.A.*, vol. 53, no. 9, pp. 1689–1699, 2013.
- [2] U. S. Energy Department, "International Energy Outlook 2017 Overview," 2017.
- [3] D. Yap, J. M. Tatibouët, and C. Batiot-Dupeyrat, "Carbon dioxide dissociation to carbon monoxide by non-thermal plasma," *J. CO2 Util.*, vol. 12, pp. 54–61, 2015.
- [4] D. Ray and C. Subrahmanyam, " CO_2 decomposition in a packed DBD plasma reactor: Influence of packing materials," *RSC Adv.*, vol. 6, no. 45, pp. 39492–39499, 2016.
- [5] S. Xu, J. C. Whitehead, and P. A. Martin, " CO_2 conversion in a non-thermal, barium titanate packed bed plasma reactor: The effect of dilution by Ar and N_2 ," *Chem. Eng. J.*, vol. 327, pp. 764–773, 2017.
- [6] M. Kano, G. Satoh, and S. Iizuka, "Reforming of carbon dioxide to methane and methanol by electric impulse low-pressure discharge with hydrogen," *Plasma Chem. Plasma Process.*, vol. 32, no. 2, pp. 177–185, 2012.
- [7] J. F. de la Fuente, S. H. Moreno, A. I. Stankiewicz, and G. D. Stefanidis, "Reduction of CO_2 with hydrogen in a non-equilibrium microwave plasma reactor," *Int. J. Hydrogen Energy*, vol. 41, no. 46, pp. 21067–21077, 2016.
- [8] C. De Bie, J. van Dijk, and A. Bogaerts, " CO_2 Hydrogenation in a Dielectric Barrier Discharge

- Plasma Revealed,” *J. Phys. Chem. C*, vol. 120, no. 44, pp. 25210–25224, 2016.
- [9] E. Y. Mora, A. Sarmiento, and E. Vera, “Alumina and quartz as dielectrics in a dielectric barrier discharges DBD system for CO₂ hydrogenation,” *J. Phys. Conf. Ser.*, vol. 687, p. 012020, 2016.
 - [10] W. C. Chung and M. B. Chang, “Review of catalysis and plasma performance on dry reforming of CH₄ and possible synergistic effects,” *Renew. Sustain. Energy Rev.*, vol. 62, pp. 13–31, 2016.
 - [11] “CO₂ reforming with methane for syngas production using a dielectric barrier discharge plasma coupled with Ni- γ -Al₂O₃ catalysts_Mei_.pdf.” .
 - [12] J. C. Whitehead, “Plasma catalysis: A solution for environmental problems,” *Pure Appl. Chem.*, vol. 82, no. 6, pp. 1329–1336, 2010.
 - [13] Y. Bai, J. Chen, X. Li, and C. Zhang, “Reviews of Environmental Contamination and Toxicology Vol 201,” vol. 201, pp. 117–136, 2009.
 - [14] T. Tsuchiya and S. Iizuka, “Conversion of Methane to Methanol by a Low-Pressure Steam Plasma,” *J. Environ. Eng. Technol.*, vol. 2, no. 3, pp. 35–39, 2013.
 - [15] L. M. Zhou, B. Xue, U. Kogelschatz, and B. Eliasson, “Partial Oxidation of Methane to Methanol with Oxygen or Air in a Nonequilibrium Discharge Plasma,” *Plasma Chem. Plasma Process.*, vol. 18, no. 3, pp. 375–393, 1998.