Plasma-enabled CO_2 methanation at ambient temperature: a trial inspired by plasma-assisted combustion

Chunyuan Zhan[1] , Shuya Xu[1] , Hyun-Ha Kim[2] and Tomohiro Nozaki[1]

[1] Department of Mechanical Engineering, Tokyo Institute of Technology, Tokyo, Japan
[2] National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan

Abstract: As CO_2 methanation is an exothermic reaction and nonthermal plasma (NTP) can provide both heat and excited species, CO_2 methanation under NTP treatment at ambient temperature becomes possible. This study realized the above process on Ru based multi-metallic catalyst. CO_2 conversion behaviors in a packed-bed dielectric barrier discharge (PB-DBD) reactor at 80 kPa were investigated. The low-temperature CO_2 methanation can be improved by applying DBD to the reaction. Besides, Ruthenium (Ru) and Lanthanum (La) play significant roles in plasma-enhanced reaction performance. To better understand reaction mechanism in DBD environment, *in situ* diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) was employed.

Keywords: nonthermal plasma, CO_2 methanation, *in situ* DRIFTS, auto-methanation

1. Introduction

To convert exhausted CO_2 into useful fuels, CO_2 methanation, also known as Sabatier reaction, can be considered as one promising way to produce high selective renewable methane with utilization of renewable hydrogen [1]. However, this reaction is affected by slow conversion speed at low temperatures because the high thermodynamic stability of CO_2 leads to a high activation barrier for its dissociation [2]. To accelerate low-temperature CO_2 conversion, nonthermal plasma (NTP) produced by dielectric barrier discharge (DBD) can be adopted because a part of CO_2 activation barrier can be removed under the impact between electron and excited CO_2 molecule activated by the plasma. It plays the similar role as it in the combustion process. When DBD is applied, it could efficiently produce methane even without external heating. This is one process intensification technique to improve the methanation process which usually requires heating at approximately 250-300 ° C, which imparts a significant advantage to the process operation from an economic viewpoint. This also implies realization of auto-methanation at ambient temperature becomes possible. Therefore, we conducted experiments to confirm the radical effect at ambient temperature. And to understand the reaction mechanism and the enhancement by NTP, *in situ* DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) was employed.

2. Experimental

Many bimetallic or multi-metallic catalysts including Ru based catalysts are widely used towards CO_2 methanation due to their good catalytic activities [3]. Ru-modified La-Ni/Al_2O_3 catalyst was employed in this study, herein expressed as “Ru(La-Ni)/Al_2O_3”. It was calcined in air at 500 °C, which is in Rasching ring type that has the dimension of 3×3 mm (diameter×height) with 1 mm hole inside. The Ni, La and Ru loadings are 11 wt%, 3 wt% and 1 wt% respectively.

As shown in **Figure 1**, the packed-bed dielectric barrier discharge (PB-DBD) reactor is a quartz tube with inner diameter of 20 mm containing catalyst pallets in a discharge region, where the high voltage electrode (6 mm o.d.) is laid at the tube center and the ground electrode is placed outside the tube. Between two electrodes DBD was generated by applying a high voltage power source (12 kHz or 100 kHz). Discharge power, kept at 45 W in this study, was determined by voltage-charge Lissajous analysis. Prior to each catalytic experiment, 13 g of catalysts were reduced at 500 °C by a constant 10 vol% of H_2/Ar stream for 1.5 h. Then the catalytic experiments were conducted at 80 kPa with temperature from 200 °C to 500 ° C. For thermal catalysis experiment, reaction temperature was measured by an infrared camera and controlled by an electrical furnace equipped with a temperature controller at a constant heating rate of 2 °C/min. H_2 and CO_2 were mixed in total flow rate of 1200 cm^3/min. And H_2:CO_2 molar ratio of 4:1 was studied. A quadruple mass spectrometer (QMS) was used for online gas measurement.

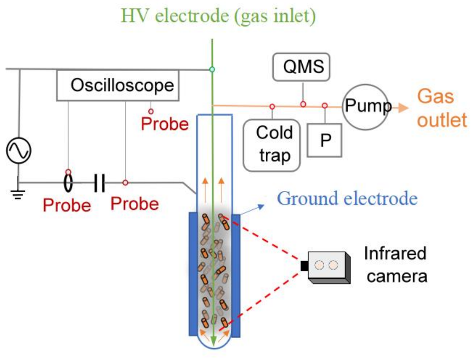

Fig. 1. Schematic diagram of experimental setup

3. Results and Discussion

The catalytic performance in this study is evaluated by the value of T_{50}, which correspond to the temperature at which 50% of CO_2 conversion is attained. We expect a lower T_{50} value when DBD is applied. **Figure 2** shows CO_2 conversion behaviors with and without plasma treatment, which compares with thermodynamic equilibrium calculated by Gibbs free energy minimization method. With DBD treatment, we maintained the ambient temperature at 20 °C, 100 °C and 200 °C respectively, the performance results in these 3 cases are the same. T_{50} is lowered from 339 °C in thermal reaction to 292 °C. This indicates the low-temperature CO_2 methanation is improved by DBD. The possible explanation is the addition of La and Ru provides more CO_2 adsorption sites and the production of vibrationally activated CO_2 can be improved in NTP [4], which are both beneficial to CO_2 adsorption process. This also confirms to our previous result that DBD type NTP can enhance CO_2 activation on La [5]. When catalyst temperature is above 400 °C, due to equilibrium limitation, the difference between thermal and plasma catalysis becomes small.

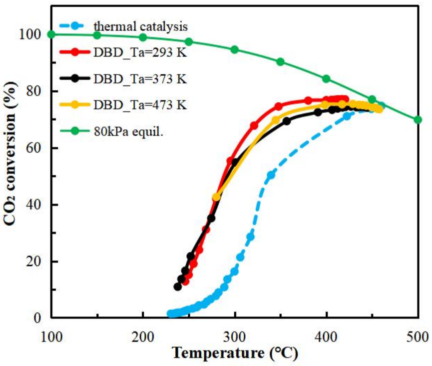

Fig. 2. Catalytic performance comparison with thermodynamic equilibrium on Ru(La-Ni)/Al_2O_3

In situ DRIFTS experiment was conducted to understand possible reaction mechanism by detecting surface species on the catalyst. The experimental observation agrees well with the reported methanation mechanisms. The most important initial step of methanation is the formation of carbonates on metal-oxide support. Carbonates are further transformed into various intermediate species such as bicarbonate (HCO_3) and formate (HCOO). This reaction pathway is categorized as the "*CO_2 associative route*" where CO_2 is associatively adsorbed as carbonate and react with surface hydrogen to form bicarbonate/formate over the support materials. Meantime, hydrogen molecules are dissociatively adsorbed on the metal surface that hydrogenates carbonate or formate consecutively towards CH_4. We would like to emphasize that La, Ni, and Ru are well dispersed and overlapped in atomic scale, indicating the interaction among surface species produced on both metal and support surfaces is efficient. Hydrogen spillover is strong on Ru which is essential for CH_4 formation [6], leading to 100% CH_4 selectivity [1]. There is a contribution of Ni for the surface hydrogen, however, the role on Ni is not as strong as Ru: CH_4 selectivity was limited to 60% at most with La-Ni/Al_2O_3. La provides active sites for anionic oxygen (O^{2-}) to react with adsorbed CO_2 [5]. In addition, La can further help adsorb CO_2 species, as well as increase the reducibility and basicity of Ni phase [7], which accelerates CO_2 conversion and explains the better performance on this catalyst. This reaction pathway is accelerated clearly by DBD.

Another important reaction pathway is "*CO_2 dissociative route*" in which CO_2 is dissociatively adsorbed on metallic catalyst surface, creating adsorbed CO; CO is further hydrogenated into formyl, then CH_4 [6]. Although adsorbed CO was not identified in our study, formyl was formed only when Ru was add to the catalyst. With more surface hydrogen supply, CH_x is generated while oxygen is dissociated as either OH or O in the proximity to it [8]; adsorbed OH and O are key to promoting carbonate formation via *CO_2 associative route*. Because neither formate nor CO was identified as intermediate species in our study, a detailed reaction pathway is hard to track from the DRIFTS observation. Meantime, carbonate formation was enhanced clearly by DBD which is a good correlation with enhanced CH_4 yield: therefore, CO_2 methanation occurs most likely via the associative route. Besides, from *in situ* DRIFTS results, we can also know activation of H_2 by DBD has a small impact on the hydrogenation of carbonate species. In other words, hydrogen spillover would be sufficiently fast without DBD. However, the role of formyl in the formation of CH_4 under the presence of DBD is not clear yet.

4. Conclusion

Ru, La, and Ni elements are well dispersed and overlapped in nanometer-scale which benefits interaction between surface species produced on each element. *In situ* DRIFTS study supports the possible reaction pathway of CO_2 methanation. The addition of La provides CO_2 adsorption sites and helps carbonate formation which is the most important step. The addition of Ru is active in hydrogen spillover, which is important to CH_4 formation. When DBD is applied, more vibrationally excited CO_2 can be produced so that CO_2 adsorption process is enhanced.

Acknowledgements

This work has been supported by JST CREST (JPMJCR19R3). C.Z. acknowledges the financial support from Tokyo Tech Academy of Energy and Informatics (ISE ID: ISE21002).

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