ISCRE25 FLORENCE 2018
BRIDGING SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Operando FT-IR analysis for methane coupling reaction to produce C2 chemicals

Jaekwon Jeoung, Juchan Kim, Jip Kim, Kyoung-Su Ha*

Department of Chemical and Biomolecular Engineering, Sogang University, Mapo-Gu, Seoul 04107, Republic of Korea

**Corresponding author: philoseus@sogang.ac.kr*

Highlights

- Non-oxidative methane coupling was conducted in a DBD plasma reaction cell
- Methane coupling reaction was analyzed via operando FT-IR method
- Characteristic peaks of intermediate species were identified and anlyzed

1. Introduction

As shown in Figure 1, we used a dielectric barrier discharge (DBD) plasma reactor cell made with insulating material and ZnSe window for an operando Fourier transform infrared (FT-IR) spectroscopy. The analysis was conducted at a reduced pressure and near room temperature. The ordered mesoporous materials (OMMs) or OMM-supported catalysts mixed with inorganic sol was coated on the ZnSe window for the operando analysis (Figure 2). During the DBD plasma reaction, absorption spectra of FT-IR were recorded about types of activated and adsorbed hydrocarbon intermediates. Through this analysis, key species for coupling reaction were identified, and the difference was also observed with or without catalytic material. In addition, the influence of plasma on the surface characteristics of particles as well as catalytic nanocrystals was investigated. Through this operando technology, the performances of plasma and catalyst were successfully assessed.

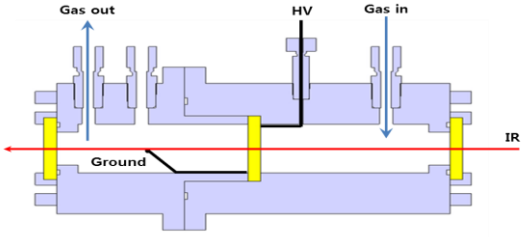

Figure 1. Reaction cell with plasma for FT-IR analysis

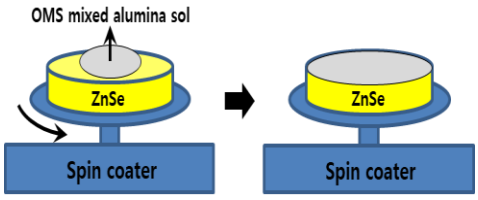

Figure 2. Spin-coated catalysts

2. Methods

OMS particles was prepared by the method explained elsewhere [1]. The structure directing agent P123 ($EO_{20}PO_{70}EO_{20}$, MW = 5800 g/mol) was mixed with aqueous HCl solution. Next, ethanol was added to the mixture and then TEOS (tetraethyl orthosilicate) was slowly added followed by mixing for 24 h. At 100 °C, the mixture was hydrothermally synthesized, followed by washing, drying and calcination. During the analysis, a feed mixture (methane 50%) was introduced to the cell under plasma. The physical properties were shown in Table 1 and Figure 3.

Sample	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)
OMS	697	1.00	6.27

Table 1. Physisorption result of OMS

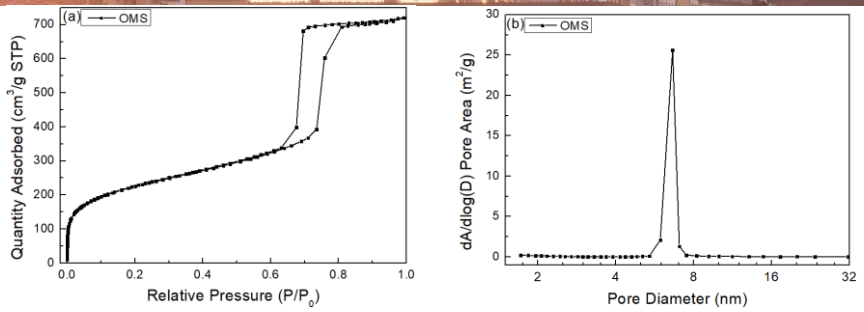

Figure 3. Physisorption result of OMS; (a) N_2 adsorption-desorption isotherm (b) pore size distribution

3. Results and discussion

In Figure 4, the peaks involved with CH_4 molecules only were observed before reaction. [2] Due to the reaction under plasma, new peaks closely related to the formation of C2 chemicals (ethane, ethylene and acetylene) appeared. [3] At 2800 – 3000 cm^{-1}, stretching vibration of CH_3 species was observed, and these species are highly related to the formation of ethane. The peak near 950 cm^{-1} was reportedly due to out-of-plane vibration, and these species are closely related to the formation of unsaturated C2 chemical, ethylene. Another peak near 730 cm^{-1} could be ascribed to the formation of acetylene, also one of the unsaturated C2 hydrocarbons. By analyzing intermediate hydrocarbon species as shown in Figure 4, the selectivities of C_2H_6, C_2H_4, C_2H_2 as well as reaction performance could be successfully predicted.

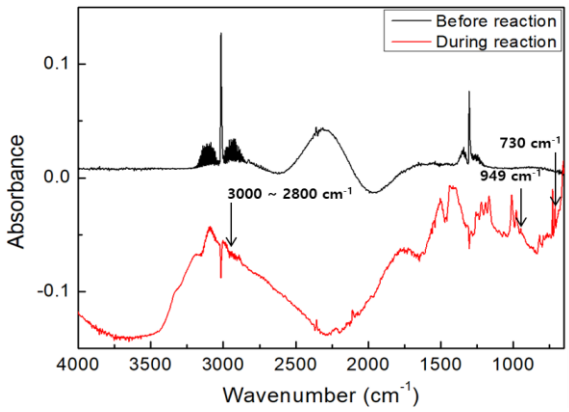

Figure 4. FT-IR spectra during reaction

4. Conclusions

By employing the operando FT-IR spectroscopy, key intermediate components were easily identified and reaction pathway of each C2 component could be predicted. Furthermore, catalytic or non-catalytic reaction in the DBD plasma cell will be tested in order to find the role of catalyst in the DBD plasma bed.

References

[1] D. Kim, G.A. Park, K.-S. Ha, "Effects of spatially restricted Ni nanocrystals within ordered mesopores on the production of syngas." Chem. Eng. J. 316 (2017) 1011-1025.

[2] Ch. Deschenaux, A. Affolter, P. Fayet, "Investigations of CH_4, C_2H_2 and C_2H_4 dusty RF plasmas by means of FTIR absorption spectroscopy and mass spectrometry." J. Phys. D: Appl. Phys. 32 (1999) 1876-7886

[3] S.A. Nair, Tomohiro Nozaki, Ken Okazaki, G.R. "In situ Fourier Transform Infrared (FTIR) Study of Nonthermal-Plasma-Assisted Methane Oxidative Conversion", Ind. Eng. Chem. Res. 46 (2007) 3486-3496

Keywords
"Operando FT-IR analysis", "Ordered mesoporous silica", "Dielectric barrier discharge plasma", "Methane coupling"