Syngas Formation by Microwave-induced Platinum/Palladium/Rhodium Spent Catalyst

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A platinum/palladium/rhodium (Pt/Pd/Rh) spent catalyst (Pt/Pd/Rh ratio of about 0.16/0.001/0.01 wt%) supported on $MgO–Al_2O_3–SiO_2$ as the main carrier was studied in the methane partial oxidation process. By utilizing the characteristics of microwave selectivity to couple with the material with high dielectric losses, micron iron powder was chosen during the microwave treatment since it has a higher dielectric constant than the Pt/Pd/Rh components. It was placed at the bottom of the reactor, where it could absorb microwave energy and convert it into heat energy, thereby enabling the partial oxidation reaction to occur. Under the same experimental conditions, namely, CH_4/air volume ratio of 1:2, microwave power of 450 W, and reaction time of 330 min, the results showed that the yields of syngas were higher when the micron iron was used with the Pt/Pd/Rh spent catalyst than when the catalyst was used alone. The yields were 67.3 and 11.6%, compared with 41.5 and 11.5%, for H_2 and CO, respectively, when using the micron iron combined catalyst rather than micron iron alone. It was also found that the coke deposed on the surface of the Pt/Pd/Rh catalyst had a filamentous shape.

1. Introduction

Syngas, which is mainly a mixture of carbon monoxide (CO) and hydrogen (H_2), is an important raw material for the chemical industry. It can be used to produce liquid fuels and chemicals with high commercial value. It is often used as feedstock in the Fischer–Tropsch process, as well as to make ammonia and methanol in the petrochemical industry.[1]

Methane is the preferred raw material for syngas production because the cost of the final product is relatively low.[2] There are generally four methods of producing syngas from methane: steam reforming, autothermal reforming, dry reforming, and catalytic partial oxidation.[3,4] Partial oxidation to syngas has gradually become a promising alternative to steam recombination,[5,6] mainly because of three advantages: (1) Partial oxidation is a mild exothermic reaction, which could save energy in industrial applications.[6,7] (2) The molar ratio of H_2 to CO is close to 2, which is an ideal feedstock ratio for subsequent processing

units such as methanol synthesis and the Fischer–Tropsch process. (3) The residence time is only a few milliseconds for the partial oxidation, which is much shorter than that of steam recombination (residence time usually in the range of 0.5–1 s); the lower cost of investment and smaller production scale could achieve the required amount of syngas production in terms of development.

Precious metal catalysts are widely used for partial oxidation reactions. Although they are more expensive than other types of catalyst, precious metal catalysts exhibit high activity and good characteristics in partial oxidation reactions (such as a relatively low carbon deposition rate). Under the same conditions, the order of conversion activity is Ph~Ru>Ir>Pt>Pd catalysts.[8] Rh and Ru catalysts have high activity and produce hardly any carbon deposits (coke). Ni catalysts are cheaper than Rh and Ru, but they deposit coke faster, leading to the rapid loss of activity of the catalyst.[9] Bitsch-Larsen *et al.* studied the partial oxidation of catalysts with noble metal catalysts.[10] The results showed that these catalysts are highly active, selectively convert methane into syngas with millisecond contact time, and form a small amount of coke.[10] Furthermore, Bhagiyalakshmi *et al.* (2010) studied the effects of catalysts, such as Pt single, Pt/Rh bimetallic, and Pt/Pd/Rh ternary catalysts, in low-temperature catalyzed methane combustion reactions (150–600 °C).[11] Their results showed that to reach the same conversion rate, the Pt/Pd/Rh ternary catalyst requires the lowest temperature, followed by bimetallic Pt/Rh, while the single metal Pt catalyst needs the highest temperature.[11]

The traditional heat treatment is usually indirect heating. Energy transfer is through convection, conduction, and radiation heat on the surface of the material, and through a thermal gradient.[12–14] Microwave energy transfer is the direct transmission of heat generated by the interaction between molecules and an electromagnetic field. The electromagnetic energy generated is converted into heat energy. The heating is fast and uniform, which is considered to be volume heating.[15–17] Microwave energy is directly converted into heat inside the material. The advantages of microwave heating include uniform and fast heating, energy saving, and a short reaction time to synthesize chemicals, as well as selective and noncontact heating.[13–16] Microwave heat treatment technology has been successfully applied in different fields, such as removing volatile pollutants,[18] oil–water separation,[19] and treatment of halogen organic pollutants with the assistance of catalysts (nanoscale zero-valent copper, iron, and titanium dioxide).[20–22]

In this study, a Pt/Pd/Rh spent catalyst combined with micron iron powder was used to produce syngas by the partial oxidation of methane. The micron iron powder with a high dielectric constant was used to absorb microwave energy to convert it into heat energy, which was used as the heat source for syngas production and help increase the yield of production.

2. Experimental Equipment and Method

2.1 Experimental equipment

A microwave oven with 2.45 GHz frequency was installed with proportional–integral–derivative (PID) control of the output power, which has a maximum of 750 W. An 80 mL quartz

glass reactor equipped with 40 small holes distributed evenly at the bottom was used. The Pt/Pd/Rh spent catalyst (approximately 0.16:0.001:0.01 wt%) was obtained from an abandoned automobile catalytic converter, which was supported on cordierite consisting of $MgO-Al_2O_3-SiO_2$ compounds, and had a 0.4 wt% coke content.

2.2   Experimental methods

One layer of ceramic fiber insulation of about 2 mm thickness was placed on the bottom of the reactor. Then, 1 g of micron iron powder (particle size, <212 μm) was spread evenly on the top of the ceramic fiber insulation. Another layer of insulation wool was laid on the top of the micron iron powder. Twelve grams of Pt/Pd/Rh spent catalyst was placed in the reactor, then it was placed in a microwave oven. The microwave power was maintained at 450 W. The experimental variables were as follows: (1) for a continuous microwave time of 330 min, mixed air and methane gas were introduced from the bottom of the reactor, and (2) the CH_4/air volume flow rate was changed from 10/10 to 10/20 (mL/min). The experimental equipment is shown in Fig. 1.

2.3   Analyses

Organic intermediates and final products were chemically analyzed using a gas chromatography–thermal conductivity detector (GC–TCD, SHIMADZU GC–2014). A tail gas sample (1 μL) was taken every 30 min with three replicates for the measurements of CO, CO_2, H_2, and CH_4. In addition, the oxygen content was calculated on the basis of mass balance using the composition results obtained by GC analysis. The carrying gas (Ar) flow rate was maintained at 25 mL/min. The oven temperature was programmed to increase from 40 to 210 °C (at which it was held for 5 min) at a ramp rate of 40 °C/min, and the GC injector temperature was 120 °C.

Carbon Determinator (Eltra, CS 800) was used to analyze the coke content of the catalyst. Images produced by a scanning electron microscope (SEM) (Hitachi, SU8000) were used to observed the surface structure of the catalyst.
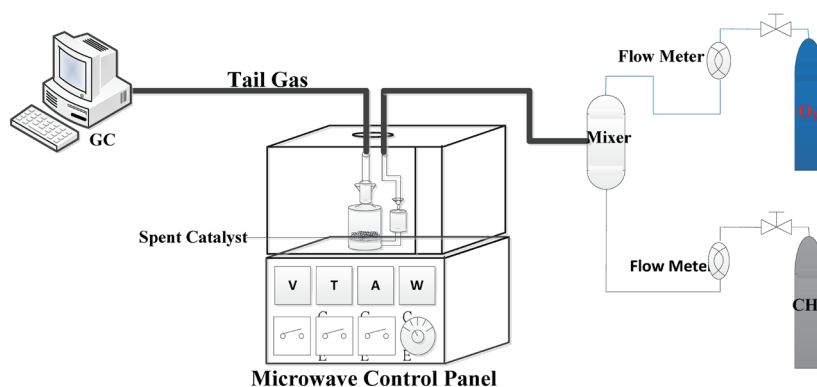

Fig. 1.   (Color online) Experimental equipment.

3. Results and Discussion

3.1 Micron iron under microwave

Micron iron is a high-dielectric-constant material (14.2 F/m) that can effectively absorb microwave energy and convert it to heat energy, and its heating rate is 109 °C/min. This heat energy can be used as a heat source for synthesis. The experiment conditions were set at the microwave power of 450 W, an exposure time of 330 min, and a volume flow ratio of CH_4/air controlled at approximately 1:1 (10/10 mL/min) or 1:2 (10/20 mL/min).

As shown in Fig. 2, the average yields of H_2 and CO are 13.1 and 12.4%, respectively, when the CH_4/air ratio was 1:1. Significant condensation was formed at the reactor outlet in the first 60 min. According to the partial oxidation mechanism, methane first oxidizes with oxygen to form CO_2 and H_2O. Under the microwave conditions, when the volume flow ratio of CH_4/air was increased to 1:2, the average yields of H_2 and CO were reduced to 11.6 and 11.5%, respectively. In the latter part of the methane partial oxidation process, the remaining methane can be regenerated and reacted with hydrogen oxide to form CO and H_2 by steam reforming and dry reforming with CO_2.

3.2 Pt/Pd/Rh spent catalyst under microwave with micron iron

As mentioned previously, micron iron can absorb microwave energy and convert it to heat energy as a heat source for the partial oxidation reaction. When utilizing the Pt/Pd/Rh spent catalyst in the process, the rate of the reaction increased significantly. Under the same microwave conditions, namely, a microwave power of 450 W, a treatment time of 330 min, and a CH_4/air ratio of 1:1 (10/10 mL/min), the results are as shown in Fig. 3 were obtained. The yields of H_2 and CO reached 40.7 and 20.7%, respectively. When the CH_4/air ratio was increased to 1:2, the yields of H_2 and CO increased to 67.3 and 41.5%, respectively. The coke content increased from 0.4 to 1.4 and 0.6%, respectively, when the CH_4/air ratio was increased from 1:1 to 1:2.
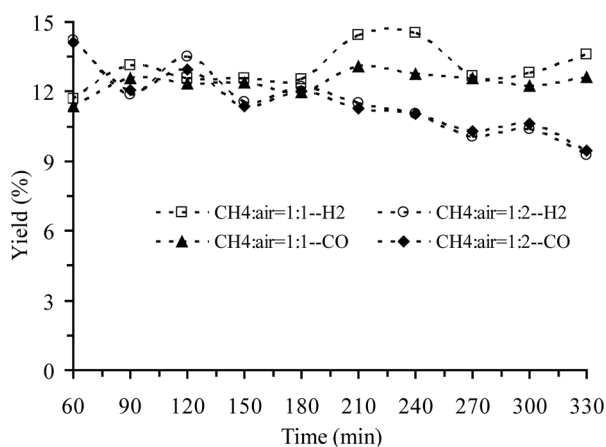

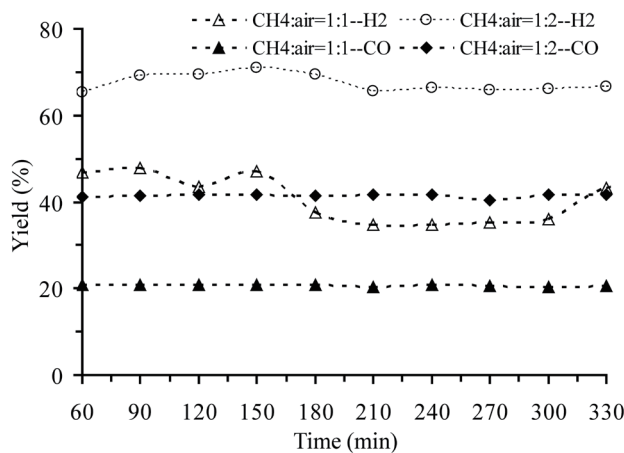Fig. 2. Yields of H_2/CO under microwave with micron iron.

Fig. 3. Yields of H_2/CO under microwave with micron iron and spent catalyst.

The reaction temperature for methane partial oxidation is usually 1300–1400 °C to achieve a high conversion rate. However, it can be achieved at a low temperature and a short reaction time when a catalyst is used.[23,24]

Under the same microwave conditions and a CH_4/air ratio of 1:2, when Pt/Pd/Rh spent catalyst was used, the mean yield of H_2 increased 5.8 times (67.3 vs 11.6%) and the mean yield of CO increased 3.6 times (41.5 vs 11.5%). This demonstrates that micron iron provides the heat source needed for the syngas production, while the Pt/Pd/Rh spent catalyst increases the rate of methane steam recombination and the dry recombination reaction, thereby increasing the H_2 and CO yields.

3.3   Structure analysis of catalyst

The Pt/Pd/Rh spent catalyst carrier was cordierite in this study, which is composed of MgO–Al_2O_3–SiO_2 compounds. The contents of elements Mg, Al, Si, Pt, Pd, and Rh were determined by energy-dispersive X-ray spectroscopy (EDS) self-evident, as shown in Fig. 4.

The catalyst activity is higher when the influent volumetric CH_4/air ratio is 1:1 under a microwave power of 450 W and a treatment time of 330 min, while the coke content of the catalyst increases from 0.4 to 1.4%. Figure 5(b) shows an image of the catalyst after microwave treatment. The coke deposited on the surface of the catalyst had a filamentous shape, which is consistent with the findings of Suelves *et al.*[25]
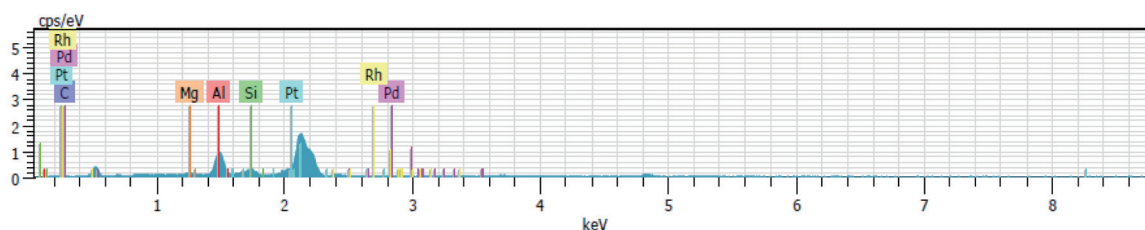

Fig. 4.   (Color online) EDS spectra of spent Pt/Pd/Rh catalyst.

(a)   (b)
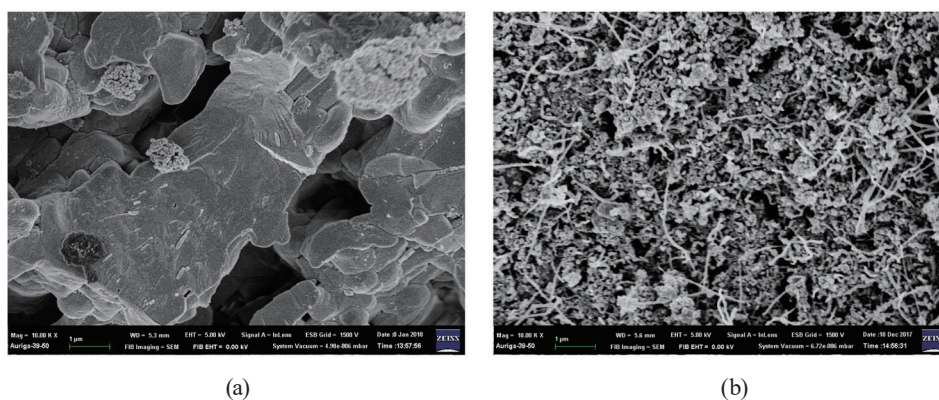
Fig. 5.   Images of spent Pt/Pd/Rh catalyst: (a) before microwave treatment and (b) after microwave treatment.

4. Conclusions

In this study, micron iron and a Pt/Pd/Rh spent catalyst were used to increase the reaction rate of methane partial oxidation to produce syngas under microwave treatment. Under the microwave conditions (CH_4/air volume ratio, 1:2; microwave power, 450 W; reaction time, 330 min), the average yields of H_2 and CO increased 5.8 times (67.3 vs 11.6%) and 3.6 times (41.5 vs 11.5%), respectively, when using the Pt/Pd/Rh spent catalyst. Furthermore, the Pt/Pd/Rh catalyst has high activity and can easily cause coke deposition. After the reaction, the coke content of the Pt/Pd/Rh spent catalyst increased from 0.4 to 1.4 wt% (CH_4/air volume ratio, 1:1), and the coke deposited on the surface of the spent catalyst had a filamentous shape. In this study, we demonstrated an innovative technology to increase the yield of syngas production by microwave induction with the Pt/Pd/Rh spent catalyst combined with micron iron.

References

1 A. Donazzi, D. Livio, C. Diehm, A. Beretta, G. Groppi, and P. Forzatti: Appl. Catal. A **469** (2014) 52. https://doi.org/10.1016/j.apcata.2013.09.054
2 M. Peymani, S. M. Alavi, and M. Rezaei: Appl. Catal. A **529** (2017) 1. https://doi.org/10.1016/j.apcata.2016.10.012
3 M. Peymani, S. M. Alavi, and M. Rezaei: Int. J. Hydrogen Energy **41** (2016) 6316. https://doi.org/10.1016/j.ijhydene.2016.03.033
4 A. G. Dedov, A. S. Loktev, D. A. Komissarenko, K. V. Parkhomenko, A. C. Roger, O. A. Shlyakhtin, G. N. Mazo, and I. I. Moiseev: Fuel Process. Technol. **148** (2016) 128. https://doi.org/10.1016/j.fuproc.2016.02.018
5 Y. Ji, W. Li, H. Xu, and Y. Chen: Appl. Catal. A **213** (2001) 25. https://doi.org/10.1016/S0926-860X(00)00887-5
6 J. H. Jun, T. H. Lim, S. W. Nam, S. A. Hong, and K. J. Yoon: Appl. Catal. A **312** (2006) 27. https://doi.org/10.1016/j.apcata.2006.06.020
7 H. E. Figen and S. Z. Baykara: Int. J. Hydrogen Energy **40** (2015) 7439. https://doi.org/10.1016/j.ijhydene.2015.02.109
8 M. Das and W. J. Koros: J. Membrane Sci. **365** (2010) 399. https://doi.org/10.1016/j.memsci.2010.09.029
9 S. Cimino, L. Lisi, and G. Mancino: Int. J. Hydrogen Energy **42** (2017) 23587. https://doi.org/10.1016/j.ijhydene.2017.04.264
10 A. Bitsch-Larsen, R. Horn, and L. D. Schmidt: Appl. Catal. A **348** (2008) 165. https://doi.org/10.1016/j.apcata.2008.06.036
11 M. Bhagiyalakshmi, R. Anuradha, S. D. Park, T. S. Park, W. S. Cha, and H. T. Jang: Bull. Korean Chem. Soc. **31** (2010) 120. doi:10.5012/bkcs.2010.31.01.120
12 M. S. Venkatesh and G. S. V. Raghavan: Biosyst. Eng. **88** (2004) 1. https://doi.org/10.1016/j.biosystemseng.2004.01.007
13 W. Klinbun and P. Rattanadecho: Appl. Math. Modell. **36** (2012) 813. https://doi.org/10.1016/j.apm.2011.07.003
14 S. S. Lam and H. A. Chase: Energies **5** (2012) 4209. doi. 10.3390/en5104209
15 M. Bhattacharya and T. Basak: Energy **97** (2016) 306. https://doi.org/10.1016/j.energy.2015.11.034
16 J. A. Menéndez, A. Arenillas, B. Fidalgo, Y. Fernández, L. Zubizarreta, E. G. Calvo, and J. M. Bermúdez: Fuel Process. Technol. **91** (2010) 1. https://doi.org/10.1016/j.fuproc.2009.08.021
17 J. P. Robinson, C. E. Snape, S. W. Kingman, and H. Shang: J. Anal. Appl. Pyrolysis. **81** (2008) 27. https://doi.org/10.1016/j.jaap.2007.07.004
18 G. Xiong, X. He, and Z. Zhang: Anal. Chim. Acta **413** (2000) 49. https://doi.org/10.1016/S0003-2670(00)00754-6
19 S. Akbari, A. H. Nour, F. Fayaz, M. S. Halimi, and A. Nazari: Aust. Basic Appl. Sci. **10** (2016) 1. https://www.researchgate.net/publication/324841241
20 C. J. G. Jou, C. L. Lee, C. R. Wu, S. C. Hsieh, and P. K. Andy Hong: Environ. Chem. Lett. **9** (2011) 355. doi: 10.1007/s10311-010-0286-y
21 C. L. Lee, C. Lin, and C. J. G. Jou: J. Air Waste Manage. **6** (2012) 1443. doi: 10.1080/10962247.2012.719579
22 C. L. Lee and C. J. G. Jou: Environ. Pollut. **1** (2012) 159. doi:10.5539/ep.v1n2p159

23 P. Aghalayam, Y. K. Park, N. Fernandes, V. Papavassiliou, A. B. Mhadeshwar, and D. G. Vlachos: J. Catal. **213** (2003) 23. https://doi.org/10.1016/S0021-9517(02)00045-3

24 G. Veser, J. Frauhammer, and U. Friedle: Catal. Today **61** (2000) 55. https://doi.org/10.1016/S0920-5861(00)00378-3

25 I. Suelves, M. J. Lázaro, R. Moliner, B. M. Corbella, and J. M. Palacios: Int. J. Hydrogen Energy **30** (2005) 1555. https://doi.org/10.1016/j.ijhydene.2004.10.006