Utilization of Waste Platinum Catalyst to Form Ethylene and Propylene by Microwave Energy

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Waste platinum (Pt) catalyst has a high carbon (coke) content, making it an excellent catalytic material for converting microwave energy into the heat energy required for ethylene and propylene formation. The dielectric constant and dielectric loss of waste Pt are 11.7 and 13.7 F/m, respectively. In this research, we use waste Pt catalyst to produce high-value gases through microwave radiation under a microwave power of 450 W and an irradiation time of 9 h with an influent volumetric C_3H_8/O_2 ratio of 1:1. The yields of H_2, ethylene, and propylene were 4.4, 22.3, and 37.3%, respectively. In addition, the density of the coke increased from 30.5 to 37.8 wt% during the microwave reaction. Therefore, the utilization of waste Pt catalyst to produce ethylene and propylene by microwave radiation can not only produce high-value gases (ethylene and propylene) but also be used as a strategy to recycle and reuse waste resources.

1. Introduction

To use energy resources more efficiently, especially in small-scale applications, catalytic partial oxidation is a promising means of producing H_2 or syngas.[1] However, there are some problems with the application of methane for partial oxidation, including difficulties in storage and transportation. Light hydrocarbons, such as propane and butane, are easy to store, disperse, and transport as sources of syngas production.[2]

Light hydrocarbons have not been widely used, mainly due to the high temperature required for the catalyst surface during pyrolysis. A high temperature causes the catalyst to sinter, making the catalyst inactive and forming coke precursors that cause the growth of coke deposits[1,3] Many reactions occur in series or in parallel during the partial oxidation of propane catalysts, including 1) partial oxidation, 2) steam and dry reforming, 3) a water-gas shift, 4) total oxidation, 5) methanation, 6) dehydrogenation, 7) carbon deposition, 8) cracking, and 9) water formation.[4,5] The by-products of reactions include methane, ethane, ethylene, acetylene,

propylene, and trace amounts of C_4^+ compounds. When the reaction temperature of the partial oxidation increases from 750 to 800 °C, the formation of methane and ethylene increases significantly. During the process, dehydrogenation and homogeneous cracking reactions occur.[6] Therefore, the reaction path depends on the reactant composition, temperature, heat transfer rate, residence time, and catalyst system.

The difference between microwave heat treatment and traditional heat treatment is the mode of energy transfer. For the traditional heat treatment, energy is usually transferred through convection, conduction, a thermal gradient, and radiation heat on the outside of the material. On the other hand, microwave heat is transmitted directly between an electromagnetic field and molecules. The generated electromagnetic energy is converted into thermal energy.[7,8] Microwave irradiation is directly converted into heat inside the material. The benefits of microwave heating are energy saving, an even and rapidly increasing temperature, a short reaction time for synthesizing chemicals, and selective and contactless heating.[9,10] Microwave heat treatment technology has been widely applied in multiple fields, including food processing, sterilization,[8] curing and ceramic preheating,[9] and the management of halogen organic pollutants accompanying catalysts (iron, titanium dioxide, and nano-zero-valent copper).[11–13]

In this study, waste Pt catalyst with a high (>25 wt%) carbon content was used to absorb microwave radiation and convert it into the thermal energy necessary for ethylene and propylene formation. This is an innovative technology from the perspectives of energy use, the circular economy, and waste catalyst reuse.

2. Experimental Equipment and Methods

2.1 Experimental equipment

The microwave oven used in this laboratory-based study was equipped with a proportional–integral–derivative controller to control the output power. The microwave frequency was 2.45 GHz with a maximum output of 750 W. An 80 ml quartz glass reactor with 40 evenly distributed small holes in the bottom was used (Fig. 1). The Pt catalyst with a high carbon content was from a catalyst restructuring process carried out in the petrochemical industry. The waste Pt catalyst
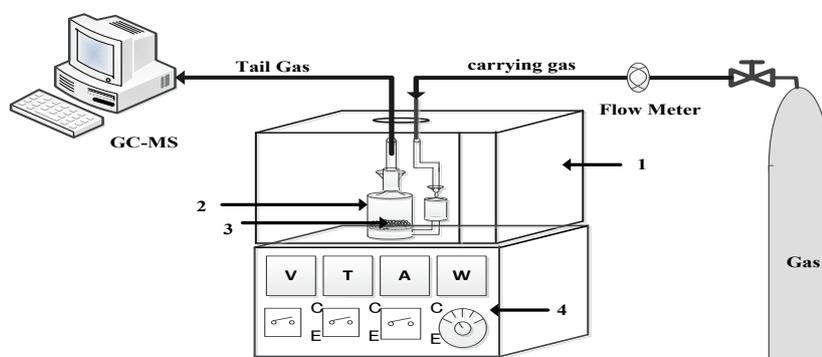
Fig. 1. Schematic diagram of experimental setup: 1. MW irradiation, 2. quartz glass reactor, 3. Pt catalyst, and 4. microwave control panel.

had a carbon content of more than 25 wt%. The Pt content was 0.3 wt%, and the Pt was in the form of particles with diameters of 1.5–1.6 mm.

2.2   Experimental methods

Twenty grams of waste Pt catalyst was placed in the quartz glass reactor, which was then placed in the microwave oven, where it was subjected to 9 h of continuous irradiation with a microwave output power of 450 W. Syngas was passed through the bottom of the reactor with an influent volumetric CH_4/O_2 ratio of 1:1 or 2:1, an influent volumetric C_3H_8/O_2 ratio of 1:1, and an influent volumetric ($C_3H_8 + H_2$, 0.9:0.1 mole%)/O_2 ratio of 1:1 (mL/min). The carrying gas (Ar) flow rate was fixed at 25 mL/min, and the oven temperature during gas chromatography (GC) was increased from 40 to 210 °C at a ramp rate of 40 °C/min and held at 210 °C for 5 min. The injector temperature during GC was set at 120 °C.

2.3   Analyses

A gas chromatography–thermal conductivity detector (GC-TCD, Shimadzu GC-2014) was used to analyze the chemical composition of organic intermediates and final products. The exhaust gas composition was analyzed by GC, with 1 μl sampled every 60 min with three replicates. In addition, on the basis of the oxygen component, the material balance was calculated utilizing the composition obtained from GC analysis.

The temperature was measured using a K-type thermocouple with an error of 0.3% over the entire temperature range. The coke content of the catalyst was analyzed using a carbon determinator (Eltra, CS 800). Images produced by a scanning electron microscope (SEM; Hitachi, SU8000) were used to observe the changes in the surface structure. An impedance analyzer (Agilent Co., 4291B) was used to measure the dielectric constant and dielectric loss of the waste catalyst at 2.45 GHz microwave frequency and 25 °C, and the measured values were 11.7 and 13.7 F/m, respectively.

3.   Results and Discussion

3.1   Effect of CH_4/O_2 influent volumetric ratio on syngas yield

The absorbed energy can be converted into thermal energy using the waste Pt catalyst for partial oxidation and the characteristic that the carbon (coke)-containing catalyst can absorb microwave radiation. For the case of microwave radiation of 450 W and an irradiation time of 9 h, the results in Fig. 2 show that when the influent volumetric CH_4/O_2 ratio was 1:1, the average yields of hydrogen and CO were 61.5 and 45.8%, respectively. The average temperature of the catalyst was 596 °C. When the influent volumetric CH_4/O_2 ratio was increased to 2:1, there was a higher methane concentration during the oxidation process. In addition, increasing the feeding speed resulted in higher energy and faster heat convection through the medium bed as well as a lower contact time for the catalyst reaction. The average yields of hydrogen and CO were 81.5 and 74.1%, respectively, and the average temperature of the catalyst increased to 636 °C.
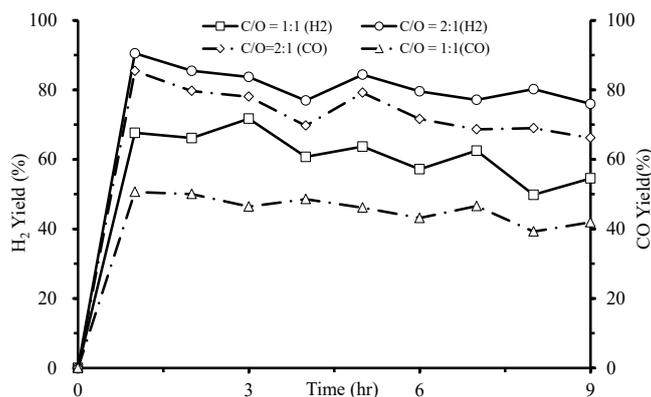
Fig. 2.　Yields of H_2 and CO for CH_4/O_2 influent volumetric ratios (C/O = 1:1 and 2:1).

3.2　Propane to ethylene and propylene

The reaction of Pt catalyst for propane partial oxidation first involves the combustion of the catalyst [Eq. (1)]. All the oxygen is consumed, then the endothermic vapors [Eq. (2)] and CO_2 are involved in the propane dehydrogenation [Eq. (3)] and the reverse water-gas shift reaction [Eq. (4)]. In addition, coupling this reaction with CO_2 through the reverse water-gas shift reaction [Eq. (4)] increased the yield of propylene.[14,15] For the case of microwave radiation of 450 W and an irradiation time of 9 h, the results in Fig. 3 show that when the influent volumetric C_3H_8/O_2 ratio was 1:1, the average temperature of the media bed was 650 °C and the yields of hydrogen, ethylene, and propylene were 4.4, 22.3, and 37.3%, respectively.

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2 \quad \Delta H_{298K} = -2046 \text{ kJ/mol} \tag{1}$$

$$C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2 \quad \Delta H_{298K} = 497 \text{ kJ/mol} \tag{2}$$

$$C_3H_8 + CO_2 \rightarrow C_3H_6 + CO + H_2O \quad \Delta H_{298K} = 164 \text{ kJ/mol} \tag{3}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{298K} = -41 \text{ kJ/mol} \tag{4}$$
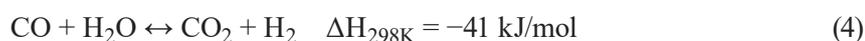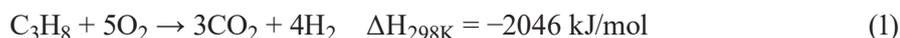
3.3　Effect of adding hydrogen to C_3H_8 on ethylene and propylene production

Propane first forms propylene through a dehydrogenation reaction and then forms electrophilic oxides on the outside of the catalyst, in the same way that O-activation cracks to form methane and hydrogen.[6,16] In addition, the reversible water-gas shift reaction [Eq. (4)] accelerates the formation of the dehydrogenation products by transforming H_2 with CO_2 into CO and H_2O while promoting the desorption of ethylene from the catalyst surface.[4] When an influent volumetric ($C_3H_8 + H_2$, 0.9:0.1 mole%)/O_2 ratio of 1:1 was used in the partial oxidation of the waste catalyst, the average temperature of the media bed was 655 °C. As shown in Fig. 4, the yields of hydrogen, ethylene, and propylene were 15.9, 32.9, and 12.1%, respectively.
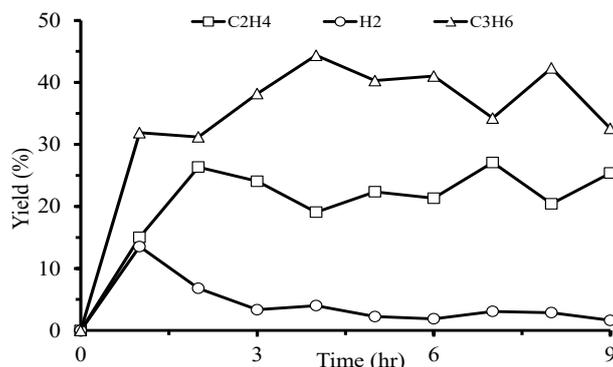
Fig. 3.   Yields of H_2, C_2H_4, and C_3H_6 for C_3H_8/O_2 influent volumetric ratio = 1:1.
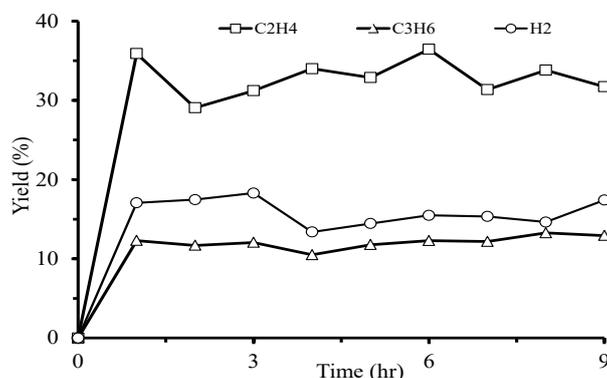
Fig. 4.   Yields of H_2, C_2H_4 ,and C_3H_6 for $(C_3H_8 (0.9) + H_2(0.1))/O_2$ influent volumetric ratio = 1:1.

In addition, a higher hydrogen pressure (feeding with hydrogen) increased the yield of methane. The results show that the yield of methane ($C_3H_8 + H_2/O_2$) was higher than that of (C_3H_8 /O_2) (20.6% vs 14.5%).

3.4   Structural analysis of catalyst

For the case of an influent volumetric C_3H_8/O_2 ratio of 1:1, an exposure time of 9 h, and microwave radiation of 450 W, the SEM images in Figs. 5(a) and 5(b) show significant differences before and after the microwave treatment, respectively. After the microwave treatment, there was a layer of coke on the outside of the spent catalyst, filling the interstices between particles. A large amount of coke was deposited during the reaction, and the coke distribution became extremely dense. Figures 6(a) and 6(b) show that the amount of coke on the outside of the catalyst was significantly increased as a result of the microwave reaction.
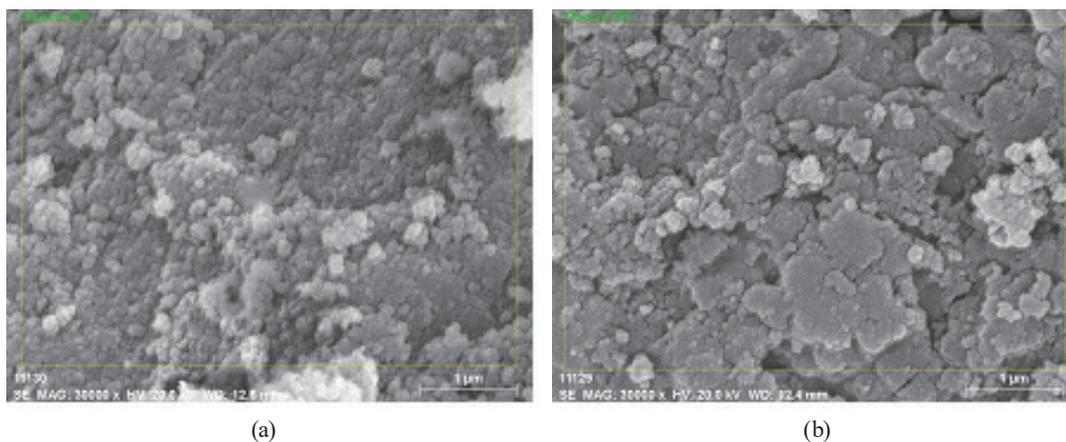
Fig. 5.   SEM images of waste catalyst (a) before and (b) after MW treatment.
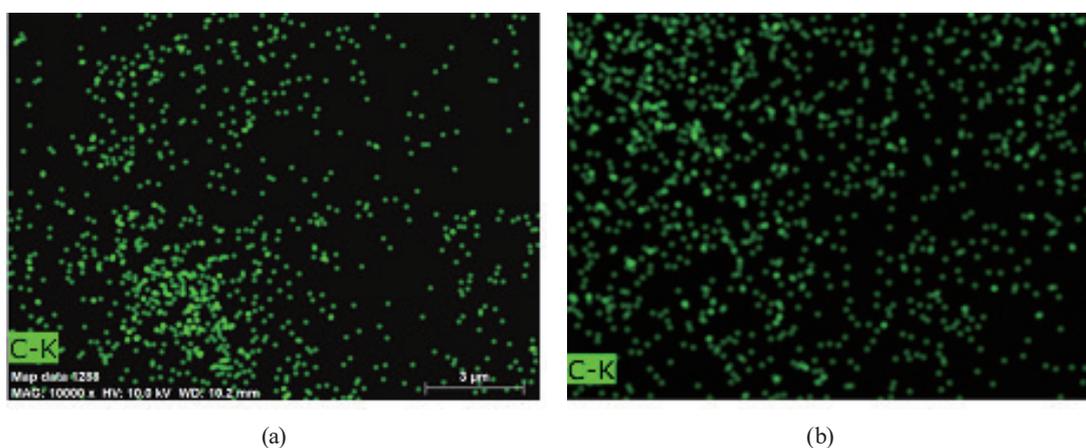
Fig. 6.   (Color online) EDS images of waste catalyst coke (a) before and (b) after MW treatment.

4.   Conclusion

In this study, the microwave radiation absorbed by a Pt catalyst with a high carbon content was converted into thermal energy used for the production of ethylene and propylene in a partial oxidation process. The results show that under microwave radiation of 450 W, an irradiation time of 9 h, and an influent volumetric C_3H_8/O_2 ratio of 1:1, the yields of hydrogen, ethylene, and propylene were 4.4, 22.3, and 37.3%, respectively. Moreover, the addition of hydrogen to the feed accelerated the reverse water-gas shift reaction and promoted the desorption of ethylene from the catalyst surface. The yield of ethylene ($C_3H_8 + H_2/O_2$) was higher than that of C_3H_8/O_2 (32.9% vs 22.3%). Ethylene and propylene are the most important intermediate products in the petrochemical industry and can be used to produce petrochemicals such as polyethylene, vinyl chloride, styrene, polypropylene, and acrylonitrile. Therefore, the production of ethylene and propylene by microwave induction from waste Pt catalysts is an innovative technology from the perspectives of energy use, the circular economy, and waste catalyst reuse.

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