Improvement of ethylene epoxidation by palladium–silver catalysts in a low-temperature dielectric barrier discharge system

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Abstract. This work was to improve the ethylene (C2H4) epoxidation reaction by adding different catalysts in a low-temperature dielectric barrier discharge (DBD) system. The studied catalysts for the ethylene epoxidation were 0.1 wt.% silver (Ag), 0.005 wt.% palladium (Pd), 0.01 wt.% Pd, and 0.01 wt.% Pd-0.1 wt.% Ag catalysts, which were coated on the second half surface of the frosted glass plates, used as a dielectric barrier material. A separate O2/C2H4 feed with a C2H4 feed position fraction of 0.5 was employed to suppress all undesired reactions and to enhance the EO selectivity. The C2H4 separate feed from O2 reduced opportunity of the collision between C2H4 molecules with high energetic electrons, causing the reduction in carbon monoxide (CO) formation, carbon dioxide (CO2) formation, dehydrogenation, C2H4 cracking, and ethylene oxide (EO) oxidation. Interestingly, the presence of any active catalyst (0.1 wt.% Ag, 0.01 wt.% Pd or 0.01 wt.%Pd-0.1 wt.% Ag catalysts) provided the significant increases in the EO selectivity due to the addition of surface reactions on the active sites of the applied catalysts. The bimetallic 0.01 wt.% Pd-0.1 wt.% Ag catalyst in the DBD system exhibited the best synergistic process performance in terms of the highest EO selectivity and yield. The addition of the Pd on the 0.1 wt.% Ag catalyst promoted the reaction of oxametallacycle (OMC) intermediate to form the desired EO and maximized the difference in the activation energies between the desired EO formation and undesired acetaldehyde formation of OMC, resulting in the improved EO selectivity.
1. Introduction
The global economic and population growths lead to the expansion of industries and petrochemicals. Ethylene oxide (C₂H₄O, EO) is one of important industrial chemicals to produce several useful chemicals such as polyethylene glycol or polyethylene oxide, which are used in surfactant and cosmetic industries. In addition, ethylene glycol produced from EO is used as an automotive coolant and antifreeze. The main consumption of ethylene glycol is for the production of polyester polymers. Moreover, EO is used in many industries: foodstuffs and medical supplies, pharmaceuticals, textiles, and adhesives [1].

The commercial process of EO production is the gas-phase partial oxidation of ethylene or ethylene epoxidation over silver (Ag)/low surface area (LSA) alumina (α-Al₂O₃) catalysts. Promoters such as rhenium, chlorine, copper, and cesium were well-known reportedly to enhance the EO selectivity [2-4]. This commercial process can provide a high EO selectivity with a low EO yield but it is required both high temperature and pressure in operation, leading to a high energy consumption. Moreover, the catalyst deactivation from coke deposit and agglomeration of the catalyst particles reduce in the long-term stability of any applied catalyst.

Non-thermal plasma (NTP), which is one kind of electric gas discharges, is a promising technique to be used for various applications such as chemical reactions, environmental remediation, biofilm treatment, and wastewater treatment [5-7]. The major advantage of this NTP over thermal plasma is the generated high energy electrons having an extremely high temperature (approximately \(10^4-10^5\) K) with a low bulk gas temperature (close to ambient temperature) [8]. Therefore, it can be operated at ambient temperature and atmospheric pressure to initiate several chemical reactions which are normally proceeded at elevated temperatures, leading to low energy consumption. Hence, the NTP was chosen in this work.

Dielectric barrier discharge (DBD) system, which is a type of the NTP, has been employed for many chemical reactions including the ethylene epoxidation. The activity of ethylene epoxidation was improved by using the frosted glass plate as a dielectric barrier material [9]. The high roughness of the frosted glass plate surface with more shape edges was responsible for generating more uniform micro-discharge with higher plasma stability. For the separate feed technique, O₂ with helium was injected throughout the DBD reactor while C₂H₄ was separately fed at the middle of the DBD reactor, in which could reduce the collision opportunity between C₂H₄ molecules and high energetic electrons, leading to decreases in undesired reactions (coupling, dehydrogenation and EO oxidation reactions) and increases in the EO selectivity and yield [9,10]. In addition, the presence of a Ag catalyst supported on glass plate significantly gave higher EO selectivity, twice as much as that of the sole DBD system [11]. An addition of promoters can improve the ethylene epoxidation activity. However, a few researches have studied the active palladium (Pd) promoter for the ethylene epoxidation in the conventional catalytic processes [12,13]. Therefore, it was of a great interest to investigate the active Pd promoter, for the first time, to be used in a dielectric barrier discharge (DBD) system for the ethylene epoxidation reaction.

This research was a continuation of our previous work that studied the ethylene epoxidation in a low-temperature parallel plate DBD system. The DBD system with a frosted glass plates were operated with a separate feed of C₂H₄/O₂ (a C₂H₄ feed position fraction of 0.5) over Ag catalysts under the base conditions [9-11]. The effect of Pd and Pd on Ag catalysts in the DBD system on the C₂H₄ epoxidation was also investigated.

2. Experimental
2.1. Materials and Chemicals
Silver nitrate (AgNO₃) with 99.9% purity and palladium (II) nitrate (Pd(NO₃)₂·2H₂O) with 40.0% Pd basis, supplied by Sigma-Aldrich, were used as Ag and Pd catalyst precursors, respectively. All chemicals used in this work were an analytical grade and used as received without further purification. The frosted glass plates with 2 mm thickness used as a dielectric barrier material as well as a catalyst support were cleaned with distilled water and acetone a few times before use. Polyoxyethylene octyl
phenyl ether (Triton-x-100, t-Oct-C₇H₇-(OCH₂CH₂)ₓOH, x= 9-10), a nonionic surfactant, supplied by Sigma Aldrich, was used to improve the wettability of the aqueous catalyst precursor solutions on the frosted glass plate surface. Helium (99.995% purity), 40% ethylene in helium (± 1% uncertainty), and 97% oxygen in helium (± 1% uncertainty), were supplied by Linde (Thailand) Public Co., Ltd.

2.2. Catalyst Preparation Method
The sequential incipient wetness impregnation method was used to prepare all studied catalysts. The AgNO₃ or Pd(NO₃)₂·2H₂O was dissolved in 3 ml of deionized water, and was then mixed with 0.05 ml of the purified Triton-x-100 solution. For both monometallic catalysts (Ag and Pd), the catalyst precursor solution was applied on the cleaned frosted glass plate to achieve different nominal loadings of 0.1 wt.% for Ag, 0.005 and 0.01 wt.% for Pd based on the cleaned frosted glass plate weight. The same impregnation method was applied for loading a second metal (Pd) on the as-calcined 0.1 wt.% Ag catalyst using the Pd precursor solution to obtain a nominal Pd loading of 0.01 wt.. For each impregnation step, the glass plate supports were dried at 383K overnight, and then calcined at 773K in an open-air furnace for 5 h.

2.3. Reaction Activity Experiments
The ethylene epoxidation experiments were performed in the parallel dielectric barrier discharge (DBD) reactor, which was operated at atmospheric pressure and ambient temperature (around 25–27°C). The schematic of experimental setup of the DBD reactor system for the ethylene epoxidation reaction is shown in Fig. 1a and the DBD reactor configuration is illustrated in Fig.1b. The reactor sizes were 2.0 cm height × 5.5 cm width × 17.5 cm length for inner dimensions and 3.0 cm height × 10.5 cm width × 24.0 cm length for outer dimensions. The gap distance between the two electrodes was fixed at 7 mm.

![Figure 1](image_url)

**Figure 1.** (a) Schematic diagram of the experimental setup of the DBD plasma system for the ethylene epoxidation reaction and (b) Configuration of the parallel plate DBD reactor with a frosted glass plate.

Alternating current (AC) applying across the electrodes generated microdischarge at an applied voltage of 19 kV and an input frequency of 500 Hz, which were previously found to be the optimum conditions [9]. The power supply system had three steps to convert a domestic AC power (220V, 50 Hz) to high voltage AC, as described previously [14]. A function generator was employed to adjust the output frequency and voltage of the high voltage AC side. The output voltage value was measured by a digital multimeter (Agilent, U1273A) with a high voltage probe (Cal Test Electronics, CT2700). An oscilloscope was used to monitor its sinusoidal wave signal, while the input power and current of the DBD system were measured by a power analyzer (Extech Instruments Corporation, True RMS Single Phase Power Analyzer, 380801).

The flow rates of ethylene (C₂H₄) and oxygen (O₂) with helium were controlled by a set of electronic mass flow controllers, supplied by AALBORG Instrument & Controls Inc., to get a desired total flow.
rate of 50 cm$^3$/min. All reactant lines had 7 μm in-line filters before passing through the mass flow controllers in order to trap any foreign particles. The reactor pressure was controlled via a needle valve. The gaseous outlet of the reactor was vented to the atmosphere via rubber tube exhaust or entered an on-line gas chromatograph (GC) to analyse the product gases. The moisture in the effluent gas was removed by a water trap before entering the on-line GC. The compositions of the feed and outlet gas were determined by the GC, equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). For the TCD channel, two pack columns (HAYESEP Q and HP-PLOT Molesieve) was used to analyze EO and O$_2$. For the FID channel, a capillary column (HP-AL/S) was used for the analysis of C$_2$H$_4$. After the feed composition was unchanged with time, the power supply was turned on to generate the discharges. The product gas composition was analysed by the GC every 15 min (at least five times). The experimental data with less than 5% error were averaged and then used to determine the ethylene epoxidation performance in terms of the C$_2$H$_4$ and the O$_2$ conversions, and the EO selectivity and yield, which were calculated from the following equations:

\[
\% \text{ Reactant conversion} = \frac{(\text{moles of reactant in} - \text{moles of reactant out}) \times 100}{(\text{moles of reactant in})}\]

(1)

\[
\% \text{ EO selectivity} = \frac{[(\text{number of carbon or hydrogen atom in product}) (\text{moles of EO produced})] \times 100}{[(\text{number of carbon or hydrogen atom in C$_2$H$_4$}) (\text{moles of C$_2$H$_4$ converted})]}\]

(2)

\[
\% \text{ EO yield} = \frac{(\% \text{ C$_2$H$_4$ conversion}) \times (\% \text{ EO selectivity}) }{100}\]

(3)

3. Results and discussion

Under the studied conditions of both the sole plasma and the catalytic-plasma systems, the chemical reactions mostly occurred in the gaseous phase, in which most of the generated electrons instantaneously collided with all gas molecules (C$_2$H$_4$ and O$_2$) to generate highly active species (metastable radicals and ions) [15]. For the combined catalyst-DBD system, the surface catalytic reactions on the metal active sites provided the additional activity.

![Ethylene and Oxygen Conversion](image)

**Figure 2.** Comparison of the DBD systems on the ethylene epoxidation performance in terms of the C$_2$H$_4$ and O$_2$ conversion

As shown in figure 2, the DBD system cooperated with the investigated catalysts provides lower C$_2$H$_4$ conversion but higher O$_2$ conversion, as compared to the DBD-alone system. This is because adsorption of C$_2$H$_4$ on the active sites reduced the number of gaseous C$_2$H$_4$ molecules for initiating the C$_2$H$_4$ epoxidation and all other reactions, resulting in the decreased C$_2$H$_4$ conversion. It was experimentally found that the O$_2$ conversion was the highest level in the 0.1 wt. % Ag-DBD system,
while the 0.01 wt.% Pd-DBD system exhibited the lowest C\textsubscript{2}H\textsubscript{4} conversion and the sole DBD system gave the lowest O\textsubscript{2} conversion. The bond dissociation energy of O\textsubscript{2} (498.34 kJ/mol) is much lower that of C\textsubscript{2}H\textsubscript{4} (682 kJ/mol); moreover, a residence time of O\textsubscript{2} (0.96 min) in the plasma zone is 2 times higher than that of C\textsubscript{2}H\textsubscript{4} (0.48 min) at the optimum C\textsubscript{2}H\textsubscript{4} feed position fraction of 0.5, leading to more collision opportunity between O\textsubscript{2} molecules and the high energetic electrons. Therefore, the O\textsubscript{2} conversion was higher than the C\textsubscript{2}H\textsubscript{4} conversion.

Figure 3 illustrates the EO selectivity and yield in the DBD system with different investigated catalysts. The synergetic effect of applied catalysts and the low temperature plasma gave an increase in the EO selectivity. The 0.1 wt.% Ag catalyst in the DBD system enhanced both EO selectivity and yield, as compared to the DBD-alone system. With increasing Pd loading, the EO selectivity markedly increased, while the EO yield slightly decreased due to the decrease in the C\textsubscript{2}H\textsubscript{4} conversion. The presence of Pd favorably promoted the surface reaction of OMC intermediate to form EO more than acetaldehyde, in which further reacted to form CO\textsubscript{2} and water [12]. Consequently, the monometallic Pd catalyst at the optimum Pd loading of 0.01 wt.% resulted in an increase in the EO selectivity, as compared to the monometallic Ag catalyst at the optimum Ag loading of 0.1 wt.%. Interestingly, the bimetallic Pd-Ag catalyst exhibited the enhancement of both EO selectivity and yield because the added Pd promoted the dissociative adsorption of oxygen. The difference in activation energies between the desired EO-forming reaction and the undesired acetaldehyde-forming reaction of OMC, leading to the improvement of EO selectivity. Our future study will discuss more details about the selectivities for by-products, chemical mechanisms, and catalyst characterization in order to obtain a better understanding of the chemical reactions.

![Figure 3](image.png)

**Figure 3.** Comparison of the DBD systems on the ethylene epoxidation performance in term of the EO selectivity and yield.

4. **Conclusions**
The ethylene epoxidation was investigated in the DBD system in the absence and presence of various catalysts under corresponding optimum metal loadings. The studied catalysts were 0.1 wt.% Ag, 0.005 wt.% Pd, 0.01 wt.% Pd, and 0.01 wt.% Pd-0.1 wt.% Ag which were loaded on the frosted glass plate, using as a dielectric barrier material and catalyst support. The EO selectivity significantly increased when the active metal catalysts were applied in the DBD system. The bimetallic 0.01 wt.% Pd-0.1 wt.% Ag catalyst in the DBD system could exhibit the highest EO selectivity and yield, as compared to the other combined catalytic-DBD systems and the DBD-alone system. In addition, the Pd at an optimum loading of 0.01 wt.% provided considerably high EO selectivity with reasonably high EO yield because the Pd active sits favorably promoted the surface reaction of OMC intermediate to form EO.
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