

Short Communication

Paired Electrochemical Synthesis of Ethylene and Oxalic Acid from Acetylene

Xiuli Song^{1,3}, Haiyan Du¹, Zhenhai Liang^{1*}, Zhenping Zhu², Donghong Duan¹, Shibin Liu¹

¹ College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Yingze West Street 79, Taiyuan 030024, Shanxi, China;

² State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taoyuan South Road 27, Taiyuan 030001, Shanxi, China;

³ Department of Chemistry, Taiyuan Normal University, Huangling Road 19, Taiyuan 030031, Shanxi, China

*E-mail: liangzhenhai@tyut.edu.cn

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Energy, pollution and cost are three significant factors which should be further studied in the process of synthesizing ethylene and oxalic acid. In the present work, ethylene and oxalic acid are synthesized from acetylene by paired electrochemical reaction which is an efficient, clean, energy-saving method. Ethylene and oxalic acid are determined using gas chromatograph (GC), fourier transform infrared radiation spectrometer (FT-IR) and ultraviolet visible absorption spectrophotometer (UV-Visible absorption). The new synthesis method will have great potential applications in coal chemical industry.

Keywords: paired electrochemical synthesis; ethylene; oxalic acid; acetylene

1. INTRODUCTION

China has abundant of coal resources but is short of oil resources, so the development of coal chemical industry will be long-term dominant [1, 2]. It is well known that acetylene is one of the most basic raw materials for lots of organic chemicals [3]. The route of coal chemical industry such as “coal → acetylene → ethylene and oxalic acid (from paired electrochemical synthesis) → many organic chemicals” is the unique idea to synthesize high value-added products from coal based chemicals. One-step production of acetylene by coal pyrolysis in thermal plasma reactor [4,5] and paired synthesis of ethylene and oxalic acid with electrochemical method are integrated in this route, then a clean, continuous and large scale production can be thoroughly realized in making efficient use of coal.

Ethylene, as one of important basic organic chemicals, has widespread applications. The production ability and level of ethylene industry have been the important symbol of measuring one country's comprehensive economic strength and the level of science and technology. Modern ethylene industry is intensive in capital and technology, and it is also one of the pillar industries to develop the national economy. A series of important oil chemical intermediates and end-products are synthesized from ethylene as raw material through a variety of ways. These products play an important role to drive the national economic development and to improve people's living standards [6]. At present, liquid gas method and cracking method are applied in ethylene production process. But some of these methods are seriously influenced by raw material market, resulting in uneven development or higher cost [7].

Oxalic acid is widely used in various fields including medicine industry, rare earth elements refined industry, synthesis of dye intermediates or other organic chemicals, textile and leather industry, and purification of metal equipments and so on. The quantity demanded of oxalic acid fluctuates with the vigorous development of related industries [8]. There are various methods to produce oxalic acid such as oxidation method, dehydrogenation method from sodium formate, coupling method from CO etc.. However, some of these methods require higher temperature and pressure, involve complex process and backward technology, cost more highly in raw materials and energy consumption, bring out serious pollution or it is very difficult to seek the raw materials [9-11].

There is no doubt that paired electrochemical synthesis of ethylene and oxalic acid from acetylene, as one mild and clean method, is an important research direction in this field and the new synthesis idea has not been reported all over the world up to now. It will have bright future. Thus, the problems mentioned above could be solved.

2. EXPERIMENTAL PART

2.1. Instruments and reagents

A direct current (DC) regulated power supply (HB17301SC, Hongbao Electric Group Co. Ltd., China) were used to synthesize ethylene and oxalic acid. UV-Visible spectrophotometer, FT-IR spectrometer and GC with a thermal conductivity detector (TCD, 180 °C) were used to characterize products' structures. The reagents purchased from some reagent plants in China are all analytical grade. The solutions are prepared using fresh double-distilled and deionized water.

2.2. Electrochemical synthesis of ethylene and oxalic acid

Ethylene and oxalic acid were electrochemically synthesized in a divided electrolytic cell with an isolating membrane. 180 mL H_2SO_4 solution ($c=3 \text{ mol}\cdot\text{L}^{-1}$) was poured into the electrolytic cell, putting Pd electrode in cathodic room and Pt electrode or Ti based oxide electrode with multivariant intermediate layers in anodic room, respectively followed by ventilating acetylene into the two rooms at the rate of $15 \text{ mL}\cdot\text{min}^{-1}$. Connect circuits ($I=0.1 \text{ A}$). H_2SO_4 solution was electrolyzed and electrolytic

products react to acetylene in their own room. And then ethylene could be produced in cathodic room and oxalic acid could be obtained in anodic room, respectively. The experimental apparatus schematic diagram of paired electrochemical synthesis of ethylene and oxalic acid from acetylene is shown in Fig. 1.

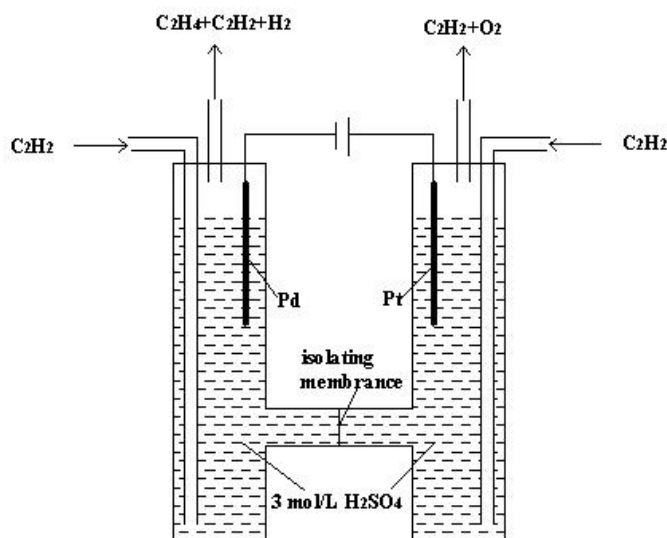


Figure 1. Experimental apparatus schematic diagram of paired electrochemical synthesis of ethylene and oxalic acid from acetylene

2.3. Characterization of ethylene

The mixture of ethylene product, acetylene and unreacted hydrogen obtained from cathodic room were ventilated into GC (SP-2100, Beijing Beifen-Ruili Analytical Instrument (Group) Co. Ltd., China), separate and detect them (Column: GDX502, 2 m, 40 °C; Carrier: N₂).

2.4. Characterization of oxalic acid

Solution obtained from anodic room is detected using UV-Visible spectrophotometer (CARY 50 Probe, VARIAN, USA, 200~800 nm) and FT-IR (Nicolet 6700, Thermo Electron Corporation, USA). The characterization results are compared with oxalic acid solution dissolved with 3 mol/L H₂SO₄ (KBr, 8 cm⁻¹, 4000-650 cm⁻¹).

3. RESULTS AND DISCUSSION

3.1. GC analysis of product

The GC chromatogram is used for detection of ethylene as shown in Fig. 2. The peak at 1.188 min. is due to ethylene. In addition, the peaks appeared at 1.508 min. and 0.165 min. are attributed to

acetylene and the unreacted hydrogen, respectively. It indicates that ethylene is produced from acetylene in cathodic room by electrochemical synthesis.

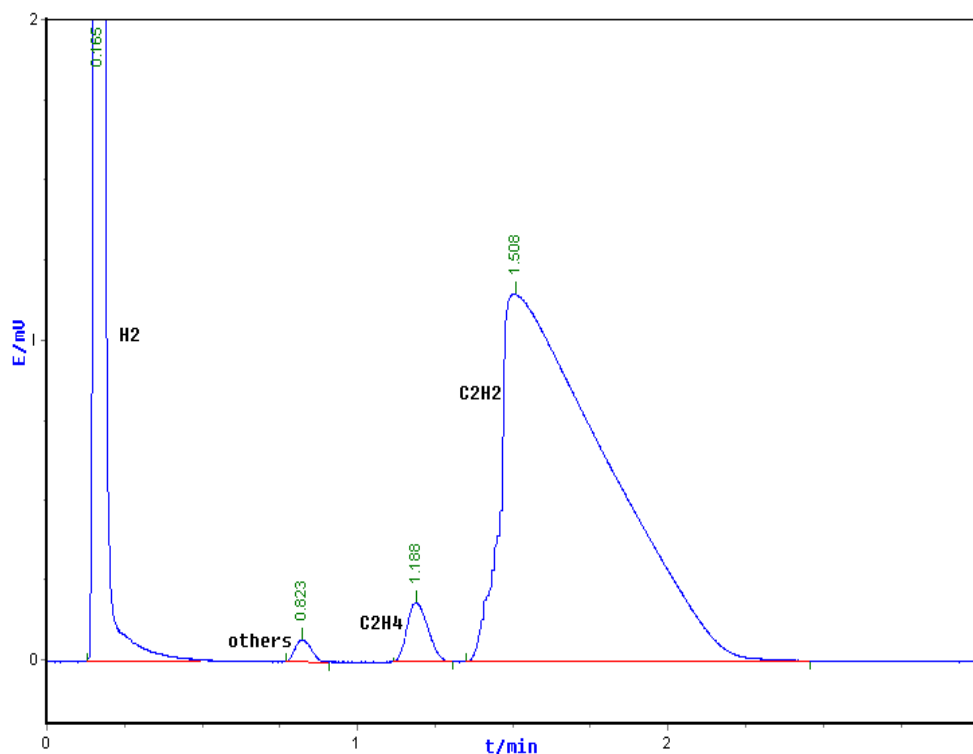
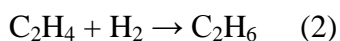
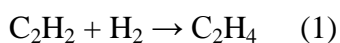


Figure 2. GC chromatogram of product obtained from cathodic room

The required hydrogen for hydrogenization of acetylene is produced by electrolyzing H_2SO_4 solution, which ensures the following two reactions take place smoothly:



Equation (1) is the desired reaction whereby acetylene is selectively hydrogenated to ethylene. At the same time, ethylene is hydrogenated to ethane in Equation (2), which leads to an unexpected reduction of the ethylene during the process. But the latter should be prevented because of the selective catalysis of Pd [12-14].

3.2. UV-Visible absorbance spectrum of oxalic acid

As shown in Fig. 3 and 4, there are two very strong absorption peaks at 205 nm, 215 nm and a weaker absorption peak at 250 nm. It indicated that the product from anodic room has the same components compared with the oxalic acid solution dissolved in H_2SO_4 ($c=3 \text{ mol}\cdot\text{L}^{-1}$). The result suggests that oxalic acid is successfully prepared from acetylene.

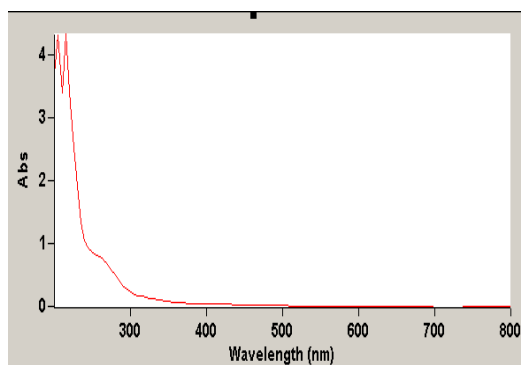


Figure 3. UV-Visible absorbance spectrum of oxalic acid solution dissolved in H_2SO_4 ($c=3$ mol/L)

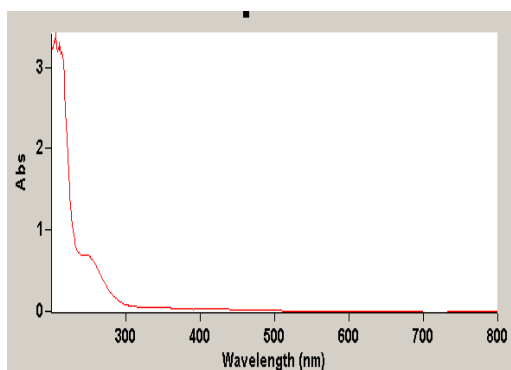
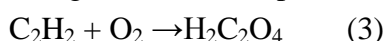


Figure 4. UV-Visible absorbance spectrum of product obtained from anodic room

The necessary oxygen for oxidization of acetylene is produced by electrolyzing H_2SO_4 solution, the following reaction takes place due to the strong oxidizing of oxygen, hydroxyl radicals etc:



3.3. FT-IR spectrum of oxalic acid

The FT-IR spectra of oxalic acid from anodic room and oxalic acid solution dissolved with $3 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$ are shown in Fig. 5. Solid oxalic acid forms double teeth dimers by hydrogen bonding from hydroxyl, the bond observed at 3440 cm^{-1} is considered to be O-H group. The bond at 1720 cm^{-1} should be designed to C=O group, and the bond observed at 1220 cm^{-1} is attributed to (C-O)+(O-C=O) of -COOH groups [15]. But for oxalic acid solution dissolved with $3 \text{ mol/L H}_2\text{SO}_4$ as shown in Figure 5, the double teeth dimers are destroyed, oxalic acid exists mainly in the form of $\text{H}_2\text{C}_2\text{O}_4$ and HC_2O_4^- , forming hydrogen bonding with water. Absorption frequency of (C-O)+(O-C=O) from -COOH groups shifts to 1330 cm^{-1} . Oxygen of C=O forms hydrogen bonding with water, which leads to that the absorption frequency of C=O shifts to 1640 cm^{-1} [16,17]. What most important is that the FT-IR spectra of the product is similar to that of oxalic acid solution dissolved with $3 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$. Thus it can be proved that oxalic acid is in-situ produced from acetylene in anodic room.

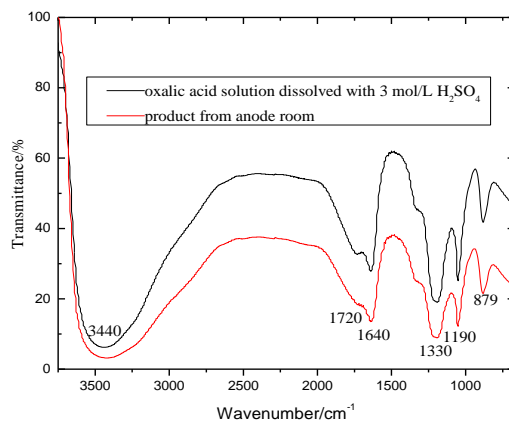


Figure 5. FT-IR spectrum of product from anodic room

3.4. Reaction mechanism

On the basis of the above results, oxidization and hydrogenization mechanism of acetylene is illustrated in Fig. 6.

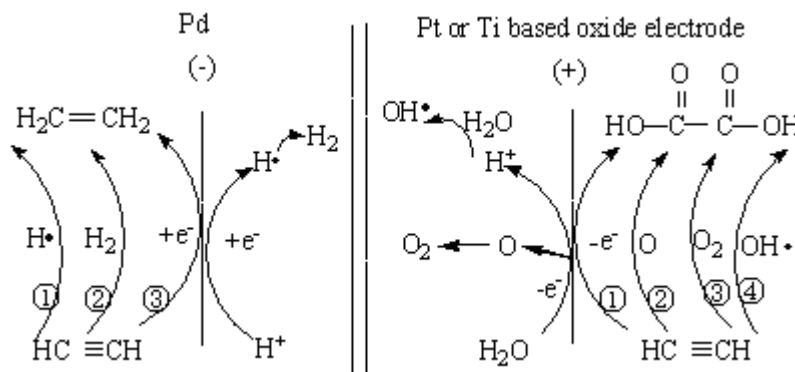
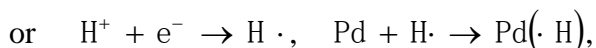
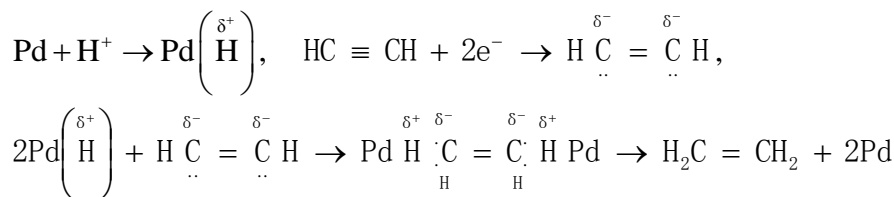
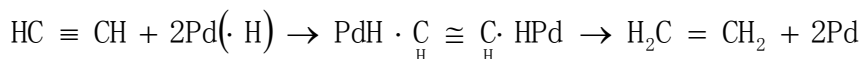


Figure 6. Reaction mechanism of paired electrochemical synthesis of ethylene and oxalic acid from acetylene

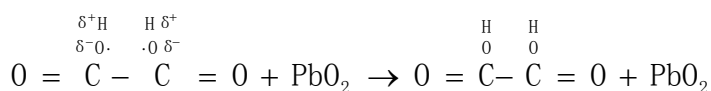
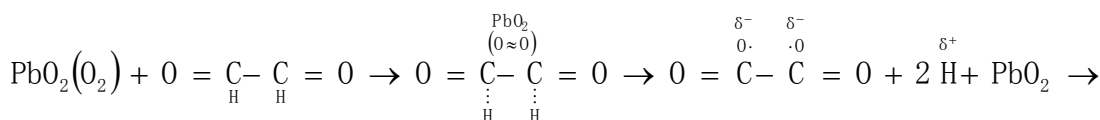
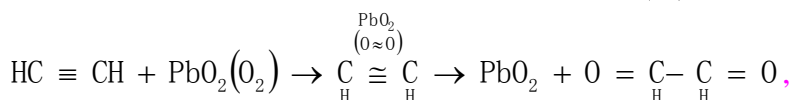
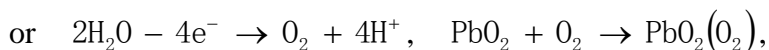
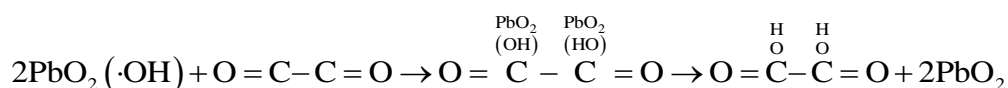
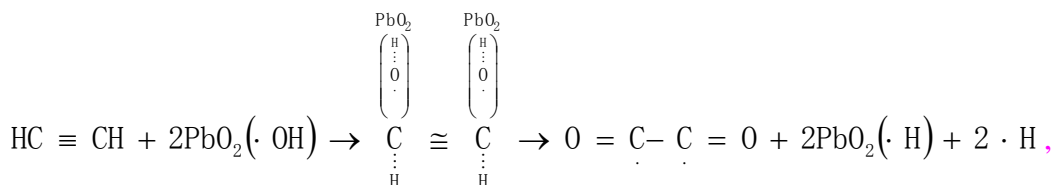
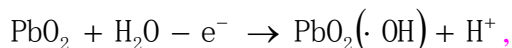
We believe that there are several routes in oxidization and hydrogenization during the process of paired electrochemical synthesis of ethylene and oxalic acid from acetylene, as following shows.

In cathode, palladium is unique in its ability to selectively hydrogenate of acetylene to ethylene [18]:





And in anode, hydroxyl radical is considered as one of the possible reasons at indirect electrochemical oxidation of acetylene. Researchers have hypothesized that hydroxyl radical can be produced by chemical oxidation of water and/or by direct oxidation of hydroxyl ions [19]:



The occurrence of each route is possible. Thus further study is required to determine which route plays the most important role.

4. CONCLUSIONS

In conclusion, it is recognized that ethylene and oxalic acid can be synthesized from acetylene with paired electrochemical method. The process will offer a new method for synthesis of ethylene and oxalic and bring bright future for coal chemical industry.

ACKNOWLEDGEMENTS

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References

1. K. C. Xie, W. Y. Li and W. Zhao, *Energy*, 35 (2010) 4349.
2. National Bureau Statistics of China. *China statistical yearbook-2005*, Beijing: China Statistics Press, 2006.
3. L. Q. Wei, *Petro. Chem. Ind. Chin.*, 44 (2009) 13.
4. C. N. Wu, B. H. Yan, L. Zhang, Y. Shuang, Y. Jin and Y. Cheng, *J. Chem. Ind. Eng. Soc. Chin.*, 61 (2010) 1636.
5. W. R. Bao, L. P. Chang and Y. K. Lv, *Proc. Safety Enviro. Prot.*, 84 (2006) 222.
6. H. Q. Tang and H. W. Xiang, *J. Fuel Chem. Technol.*, 29 (2001) 97.
7. Z. M. Liu, C. L. Sun, G. W. Wang, Q. X. Wang and G. Y. Cai, *Fuel Proc. Technol.*, 62 (2000) 161.
8. A. M. Li, J. X. Xie and Z. Li, *J. Taiyuan U. Technol.*, 31 (2000) 191.
9. Y. N. Kukushkin, V. V. Kobzev and L. P. Morozova, *Zh. Obshch. Khim.*, 42 (1972) 1609.
10. A. M. Li, Y. B. Li, S. Y. Geng and P. Z. Song, *Coal Chem. Ind.*, 18 (2006) 58.
11. S. W. Gong and J. F. Chen, *Guangdong Chem.*, 38 (2011) 75.
12. F. M. Mckenna and J. A. Anderson, *J. Catal.*, 281 (2011) 231.
13. A. Pachulski, R. Schödel and P. Claus, *Appl. Catal. A-Gen.*, 400 (2011) 14.
14. I. Y. Ahn, W. J. Kim and S. H. Moon, *Appl. Cata. A-Gen.*, 308 (2006) 75.
15. S. L. Yu, Y. W. Li and X. Q. Xia, *Spectr. Anal. [M]*. Chongqing: Chongqing University Press, (1994) 42.
16. H. P. Tang, M. D. Yang and P. J. He, *Chinese J. Process Eng.*, 2 (2002) 506.
17. S. P. Chen, T. Huang, Q. Zhang, H. Gong and S. G. Sun, *Fine Chem.*, 20 (2003) 91.
18. P. A. Sheth, M. Matthew and C. M. Smith, *J. Phys. Chem. B*, 107 (2003) 2009.
19. L. Li and R. K. Goel, *J. Hazardous Mater.* 181 (2010) 521