

아세틸렌 수소화 반응용 Pd촉매의 에틸렌 선택도 및 비활성화 특성

김정환, 김우재, 안인영, 문상흡
서울대학교 응용화학부

The ethylene selectivity and the deactivation behavior of Pd catalysts in acetylene hydrogenation

Jung-Hwan Kim, Woo Jae Kim, In Young Ahn, and Sang Heup Moon

School of Chemical Engineering and Institute of Chemical Processes, Seoul National University

Introduction

The selective hydrogenation of acetylene in ethylene rich stream is an important industrial process for purifying ethylene, which is used as a feed for the polymerization process. Pd catalyst is widely used due to its excellent activity in alkyne hydrogenation[1]. But, its selectivity for ethylene and deactivation behavior need further improvement, for which various metals or metal oxides have been added to Pd catalysts as promoters[2,3].

In acetylene hydrogenation, acetylene may undergo polymerization, which leads to the production of C4 compounds or higher hydrocarbons (green-oil). The accumulation of hydrocarbons gives rise to a reduced overall activity and the deactivation of Pd catalyst. In this study, we modified the Pd catalyst with a promoter and observed the promoter effect, particularly in the relation to the catalyst deactivation.

Modified Pd catalysts were prepared by an excess wetness impregnating method and their performance in acetylene hydrogenation was evaluated under different conditions. The surface of the catalysts was characterized by H₂-Chemisorption, thermal gravity analysis(TGA), and by monitoring the amount of C4 species produced during the reaction.

Theory

The major reason for the deactivation of Pd catalysts is the accumulation of coke such as green-oil on the Pd surface[4]. Asplund[5] studied the effect of coke formation on the intraparticle mass transfer. The accumulation of large amounts of coke was found to block the catalyst pores and induce mass transfer limitations, which were not observed on a fresh catalyst. Green-oil or carbonaceous species deposited on the catalyst surface consisted of paraffins and olefins ranging from about C8 to C24 with the H/C ratio of about 1.9[6]. According to other groups, several factors influence the formation of coke and C4 species, which are precursors of green-oil. Some groups[7] reported that the coke concentration decreases with increasing hydrogenation pressure. Battiston et al.[7] found that the concentration of carbon on the catalyst increased with decreasing H₂/C₂H₂ ratio. However, the coke formation was negligible when no hydrogen was included in the feed. Sarkany et al.[8] changed the hydrogen coverage of the Pd surface by using different CO concentrations in the gas feed while maintaining the hydrogen partial pressure constant. They observed that the C4 formation changed showing a maximum with an increase in the CO concentration. Querini[9] studied the effect of the location and the structure of coke on the kinetics of coke burning and the aging behavior of the catalysts. Considering the previous results, we can speculate that the formation and the type of green-oil or C4 species are significantly affected by several reaction conditions.

Experiment

1wt% Pd/SiO₂ was prepared by an ion-exchange method using Pd(NH₃)₄(OH)₂ as a Pd precursor. SiO₂ was added to an aqueous Pd(NH₃)₄(OH)₂ solution for the Pd-ion exchange. After being stirred for 2 hours, the suspension was centrifuged and washed with water. The catalyst was then dried at 110°C overnight and calcined in air at 300°C for 2 hours. Modified catalyst was prepared by impregnating 1wt% Pd/SiO₂ with a promoter. The atomic ratio of promoter metal to Pd was adjusted to 1.0. The catalyst was then calcined in air at 300°C for 2 hours and reduced in H₂ at either 300°C or 500°C for 1 hour before use in the reaction.

Acetylene hydrogenation was performed in a pyrex microreactor at ambient pressure. A gas mixture containing 5.2% acetylene in ethylene was allowed to flow through a reactor, which was maintained at 70°C or 90°C, and reaction products were analyzed with an on-line gas chromatograph (HP model 6890 with FID). The H₂/Acetylene ratio was adjusted to 0.5. The reaction conditions described in the above are severe enough to accelerate the deactivation of Pd catalysts in acetylene hydrogenation. Chemisorption measurements were made with ASAP2010 (Micromeritics) by using H₂ as a probing gas.

The accumulated amount of green-oil on the spent catalysts was measured by using TG (TA Instruments, TGA2050). The catalysts were deactivated to the same extent, i. e., the catalysts were used for converting the same amounts of acetylene. Temperature was raised from 30°C to 800°C at a rate of 10°C/min, and the flow rate of air was 40cc/min.

Results and discussion

In Fig. 1, the effect of metal oxide addition to the Pd catalyst is shown with respect to the catalyst deactivation behavior. To compare the deactivation rates of Pd/SiO₂/300°C (Pd only catalyst reduced at 300°C) and modified Pd/SiO₂/500°C (modified Pd catalyst reduced at 500°C), we plotted the normalized conversions for the two catalysts versus the accumulated amount of converted acetylene instead of the time-on-stream. So, the comparison is made based on the same load of the reaction. It is clear that the deactivation rate of Pd/SiO₂/300°C is much faster than that of modified Pd/SiO₂/500°C. That is, the deactivation behavior is retarded when the Pd surface is modified with the promoter. To compare the amount of green-oil on two catalysts, TGA experiment was performed. We can confirm from TGA results in Fig. 2 that the weight loss of the modified catalyst is less than that of Pd only catalyst. This result implies that the added metal oxide suppresses the formation of green-oil on the Pd catalyst. In Fig. 3, the deactivation behaviors of two catalysts are compared for different reaction temperatures. In the case of Pd only catalyst, the deactivation rate becomes faster as the reaction temperature is raised from 70°C to 90°C. But, the deactivation rate of the modified catalyst is almost constant independent of the temperature difference. Fig. 4 shows the deactivation rates of two catalysts when the reactants are diluted with inert gas (N₂), such that the mean residence time of the reactants becomes shorter. The deactivation rate of the Pd only catalyst is lowered when the reactants are diluted with N₂, but the rate of the modified Pd catalyst is unaffected by the N₂ dilution. Based on the results described in the above, we can conclude that the deactivation behavior of the Pd only catalyst is very sensitive to the reaction condition but the behavior becomes less sensitive when a promoter is added to the catalyst.

To examine the relation between the deactivation behavior and the amount of green-oil accumulated on the catalyst, we monitored the mole percentages of C₄ species (t-2-butene,

c-2-butene, 1-butene and 1,3-butadiene), which are produced during the reaction and believe to be the precursors of green-oil. In Fig. 5, during the initial period of the reaction, the total amount of C4 species produced on Pd/SiO₂/300°C is greater than that on modified Pd/SiO₂/500°C. This result suggests that the metal oxide reduces the generation of C4 species. In the case of Pd/SiO₂/300°C, the total amount of C4 species decreases with the accumulated amount of converted acetylene, which is due to the consumption of C4 species used for the formation of green-oil. On the other hand, the total amount of C4 species produced on modified Pd/SiO₂/500°C is almost constant over all ranges of converted acetylene amounts. These phenomena are due to the suppression of C4 species polymerization on the modified catalyst. The metal oxide reduces the adsorption strength of green-oil precursor on the Pd surface. Table. 1 lists the amount of H₂ adsorbed on the catalysts reduced at two different temperatures. The amount of H₂ adsorbed on modified Pd/SiO₂ is smaller than that on Pd/SiO₂, which is due to the decoration of the Pd surface with the added metal oxide. In the case of modified Pd/SiO₂/500°C, the extent of decrease in the H₂ uptake is remarkable. This phenomenon is a typical result of the SMSI effect. H₂-Chemisorption results indicate that the adsorption strength of hydrogen is reduced by the addition of metal oxide. In summary, the effects of metal oxide addition can be explained in two aspects. First, the added metal oxide suppresses the formation of C4 species on the Pd surface. Second, it suppresses the polymerization of C4 species produced during the reaction. These results agree with not only the results of TGA but also those of H₂-Chemisorption, which indicate that the selectivity for unsaturated hydrocarbons is improved because metal oxide has modified the Pd surface. Finally, the deactivation extent of catalysts can be estimated by monitoring the total amount of C4 species.

Conclusion

In this study, we observed that the deactivation behavior is improved when the Pd catalyst is modified with a metal oxide followed by a consecutive reduction at high temperature, e. g., 500°C. The improvement in the deactivation behavior is due to the decoration of the Pd surface with metal oxide. The deactivation behavior of Pd catalysts for acetylene hydrogenation is dependent on reaction conditions and can be estimated by monitoring the total amount of C4 species produced during the reaction.

Acknowledgement

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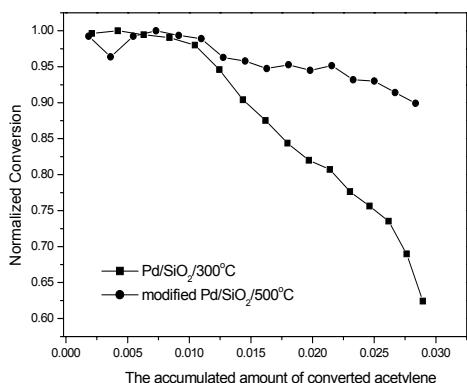


Fig.1 Deactivation reaction results on Pd/SiO₂ and Modified Pd/SiO₂

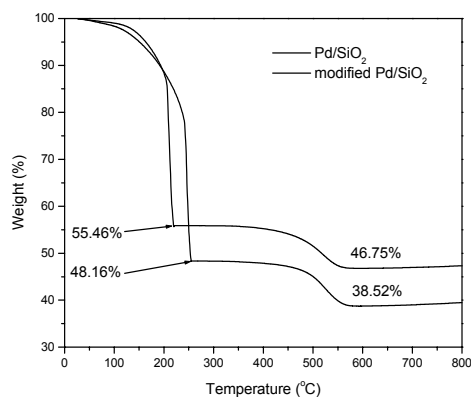


Fig. 2 TGA results in air on Pd/SiO₂/300°C and modified Pd/SiO₂/500°C

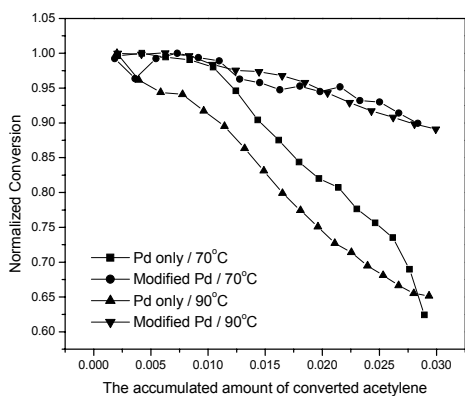


Fig.3 The deactivation rate of two catalysts at 70°C and 90°C

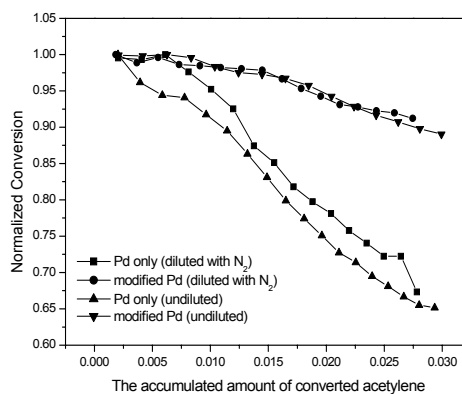


Fig. 4 Dilute effect on deactivation rate of two catalysts

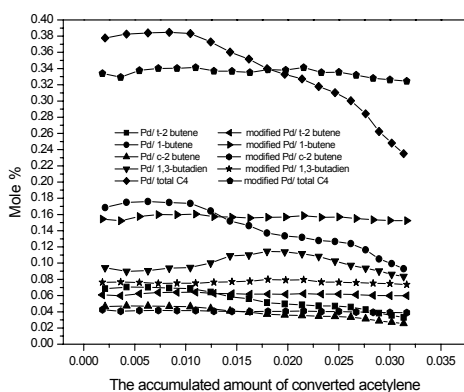


Fig.5 C4 species produced in deactivation test on Pd/SiO₂/300°C and modified Pd/SiO₂/500°C

Table 1. The amount of H₂ adsorbed on different catalysts

Catalysts	Reduction Temp.	H/Pd
Pd/SiO ₂	300°C	0.48
Modified Pd/SiO ₂	300°C	0.22
Modified Pd/SiO ₂	500°C	0.17