# 아세틸렌의 선택적 수소화 반응을 위해 변형된 $Pd/SiO_2$ 촉매의 비활성화 특성

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# Deactivation Behavior of Modified $Pd/SiO_2$ Catalyst for the Selective Hydrogenation of Acetylene

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## Introduction

Selective semi-hydrogenation of acetylene in ethylene is an industrial process of vital importance[1,2]. In the thermal steam cracking process, producing ethylene, acetylene that is a poison in the ensuing process of ethylene polymerization is also formed. This impurity is removed in selective hydrogenation process, which is usually performed on a supported palladium catalyst[3]. In order to improve the ethylene selectivity, i.e., to decrease the ethane formation from both acetylene and ethylene, 800-2000ppm CO is added to the reactants. The presence of CO decreases the acetylene conversion and influences the oligomer formation[4].

In addition to hydrogenation, acetylene undergoes hydropolymerization, leading to liquid polymer mixtures("green oil") and the deposition of carbonaceous species on the catalyst surface[5]. Such liquid fractions have been found to consist of paraffins and olefins ranging from about C8 to C24 with an H/C ratio of about 1.9. In industrial operation, the coke formation results in a reduced overall activity as well as an increased selectivity for the undesired ethane[6].

The intrinsic ability of palladium can be further improved by promoters(modifiers) and additives[7]. In this study, we added promoter to $Pd/SiO_2$ catalyst to decrease coke formation. The present work aims at clarifying the coke composition and the effect of coke on the catalyst performance for two catalysts: modified and un-modififed $Pd/SiO_2$.

## Experimental

1wt% $Pd/SiO_2$ was prepared as a reference catalyst by an ion-exchange method using $Pd(NH_3)_4(OH)_2$ as a Pd precursor following a procedure in literature[8]. Modified $Pd/SiO_2$ was prepared by incipient wetness impregnation method. The atomic ratio of promoter metal to Pd was adjusted to 1.0.

The catalysts were tested for acetylene hydrogenation in an atmospheric quartz reactor. The reaction temperature was 90℃, the reactant stream contained 5.1% acetylene in ethylene, and The $H_2$/acetylene ratio in the reaction stream was 0.5. Reaction products were analyzed with an on-line G.C. using a capillary column.

Catalysts used for the same accumulated conversion of acetylene were analyzed thermogravimetrically in air flowing at 40ml/min. The temperature was raised from 30℃ to 850℃ at a rate of 10℃/min. Prior to TPO experiments, deactivation tests were performed with two catalysts, and the deactivated catalysts were cooled to room temperature for 1 hour under $N_2$ condition. The catalysts were flushed with helium for the removal of weakly adsorbed species. The TPO experiment was conducted by raising temperature from 30℃ to 800℃ at a rate of 16ml/min in flowing 100% $O_2$. The effluent gas was analyzed by a mass spectrometer.

## Results and Discussion

Pd/$SiO_2$ was reduced at 300℃, and modified Pd/$SiO_2$ was reduced at 500℃ because these temperatures were the conditions to provide the catalysts with a high activity according to a previous study[9]. To compare the deactivation behaviors of Pd/$SiO_2$ and modified Pd/$SiO_2$, we have plotted the normalized acetylene conversion versus the accumulated amount of converted acetylene instead of plotting versus the time-on-stream, such that the comparison is made based on the same load of the reaction. Fig. 1 shows that the hydrogenation of two catalysts decreased as the amount of converted acetylene increased. The deactivation rate of Pd/$SiO_2$/300℃ is much higher than that of Pd-X/$SiO_2$/500℃. So, it is apparent that the catalyst deactivation is retarded when the catalysts are modified with a promoter.

The mole percentages of C4 species produced in the deactivation experiments are plotted in Fig. 2. C4 species include isobutane, n-butane, t-2-butene, 1-butene, isobutylene, c-2-butene and 1,3-butadiene. Pd-X/$SiO_2$/500℃ produced a larger amount of C4 species than Pd/$SiO_2$/300℃. However the amount of the C4 species decreased more rapidly on Pd/$SiO_2$/300℃ than on Pd-X/$SiO_2$/500℃. So the decrease of detected C4 species may be related to coke formation on the catalyst surface.

TGA curves in Fig. 3 deviate from each other at temperatures above 250℃, which occurs mostly due to the difference in the burn-off amount of green oil deposited on the catalysts. Pd/$SiO_2$/300℃ lost the initial weight by about 58.9% while Pd-X/$SiO_2$/500℃ lost by 44.4%. To further study the properties of green oil removed in the oxidation process, we differentiated the TGA curves to obtain the DTGA results given in Fig. 4. Three major peaks are observed in different temperature regions: below 300℃, 300℃-500℃, and above 500℃. According to Larsson et al.[10], who obtained results similar to this study in their analysis of coke by temperature-programmed oxidation(TPO), the peak below 300℃, designated as Peak I in Fig. 4, is due to heavy hydrocarbons that are adsorbed on the catalyst surface or adsorbed in the catalyst pores. Peak II observed between 300℃ and 500℃ represents coke on or in the vicinity of Pd, and Peak III above 500℃ indicates coke produced on the support without the influence of Pd. Two changes are notable in Fig. 4 as a result of the promoter modification: peak shift to lower temperatures, which is particularly large with Peak III, and characteristic changes in the intensity of three major peaks. The intensity of Peak II was significantly decreased due to the modification. The shift of Peak III may occur either because coke, or green oil, produced on the catalyst becomes more volatile, with lower molecular weight, or because the coke particles are present in smaller sizes on modified Pd/$SiO_2$. With reference to the study of Larsson et al.[10], we performed deconvolution of DTGA results obtained for two catalysts. Figs. 5 and 6 show that on modified Pd/$SiO_2$, coke burns off at lower temperatures than on Pd/$SiO_2$. The temperatures obtained by deconvolution of the peaks are summarized in Table 1.

To estimate the amount of coke and compare the characterstics of coke, TPO was additionally performed. Mass spectrometer was used to monitor $CO_2$ because coke on the catalysts reacted with $O_2$ to produce $CO_2$ and CO. Fig. 7 shows the profiles of $CO_2$ and CO obtained while the catalysts were heated. Modified Pd/$SiO_2$ produces less amounts of $CO_2$ and CO compared with the case of Pd/$SiO_2$. Furthermore $CO_2$ and CO are produced at lower temperatures on modified Pd/$SiO_2$ than on Pd/$SiO_2$. These results are in accordance with the above DTGA results indicating that coke is produced in less amounts and more volatile on modified Pd/$SiO_2$ than on Pd/$SiO_2$.

## Conclusions

The deactivation behavior of Pd/$SiO_2$ catalyst in acetylene hydrogenation is improved when the catalyst is modified with a promoter. The modification reduces the amount of green oil produced on the catalyst and makes green oil, particularly the species produced on or in the vicinity of Pd, more volatile such that it is removed at relatively low temperatures.

## Ackmowledgements

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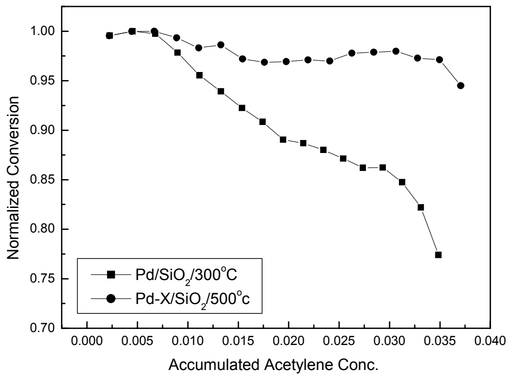

Fig. 1 Deactivation reaction results on Pd/$SiO_2$/300℃ and modified Pd/$SiO_2$/500℃

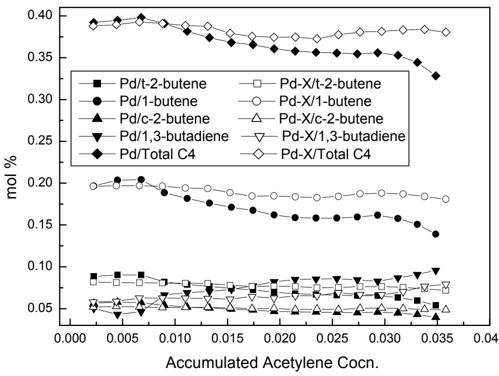

Fig. 2 C4 stream produced in deactivation reaction tests on Pd/$SiO_2$/300℃ and modified Pd/$SiO_2$/500℃

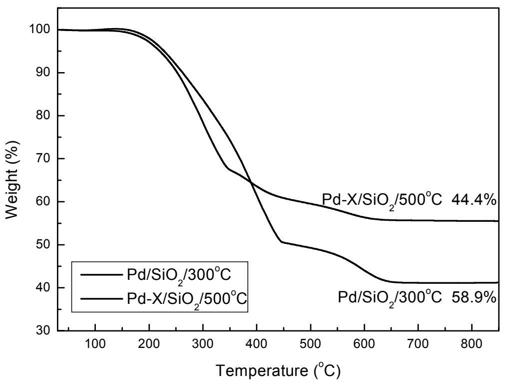

Fig. 3 TGA results in air on Pd/SiO$_2$/300℃ and modified Pd/SiO$_2$/500℃

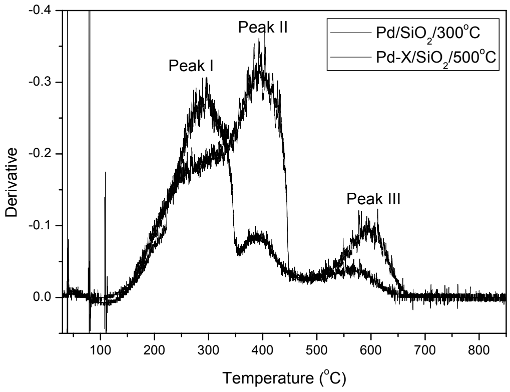

Fig. 4 DTGA results in air on Pd/SiO$_2$/300℃ and modified Pd/SiO$_2$/500℃

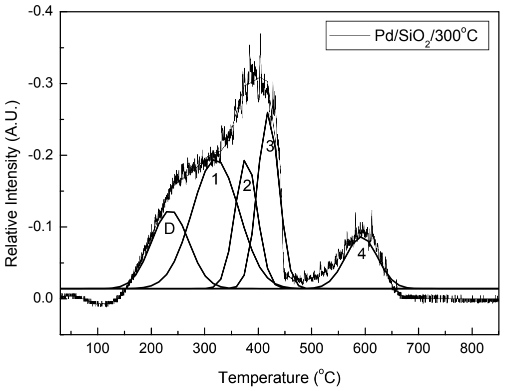

Fig 5. DTGA deconvolution on Pd/SiO$_2$/300℃

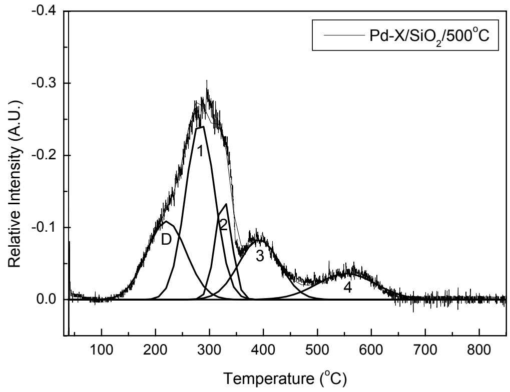

Fig 6. DTGA deconvolution on modified Pd/SiO$_2$/500℃

Table 1 Temperatures of DTGA deconvolution peak

| Peak Assign | D | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| Pd/SiO2/300℃ | 235℃ | 320℃ | 378℃ | 419℃ | 593℃ |
| Pd-X/SiO2/500℃ | 220℃ | 283℃ | 326℃ | 392℃ | 554℃ |

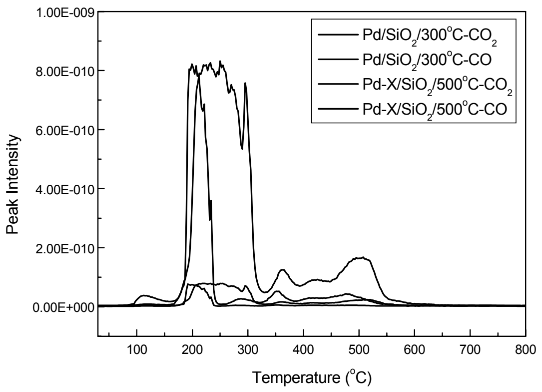

Fig. 7 TPO results in O$_2$ on Pd/SiO$_2$/300℃ and modified Pd/SiO$_2$/500℃