Selective Hydrogenation of Acetylene on La- and Nb-modified Pd/SiO₂ Catalysts

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ABSTRACT
The performance of Pd/SiO₂ catalysts modified with La and Nb oxides in the selective hydrogenation of acetylene was investigated. The amounts of H₂ chemisorbed on the catalysts were significantly reduced when the catalysts were reduced at high temperatures, e. g., 500 °C. This is because the Pd surface is covered with small patches of partially reduced La and Nb oxides after the high temperature reduction, which is the characteristic of a well-known strong metal support interaction (SMSI) phenomenon. X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) results indicated that the Pd surface was also modified electronically, such that the adsorption of ethylene to the Pd surface was weakened. Such behaviors of metal oxides affected the ethylene selectivity and lifetime of the catalysts. The ethylene selectivity of Pd-La/SiO₂ and Pd-Nb/SiO₂ was improved due to the geometric and electronic modifications of Pd by the oxides. Pd-La/SiO₂ showed more significant improvement in the ethylene selectivity than Pd-Nb/SiO₂. The activity of Pd-Nb/SiO₂ was comparable to that of Pd/SiO₂, even though the Pd surface was partially covered with Nb oxide, because the oxide had an additional hydrogenation activity. The catalyst deactivation was also retarded when the Pd surface was modified with La and Nb oxides.

Thermogravimetric analysis (TGA) and temperature-programmed oxidation (TPO) results showed that Pd-La/SiO₂ and Pd-Nb/SiO₂ produced less amounts of coke and the coke species were more volatile than in the case of Pd/SiO₂.

KEY WORDS
acetylene hydrogenation, palladium, promoter, ethylene selectivity

INTRODUCTION
The selective hydrogenation of acetylene in ethylene, which is used for removing trace amounts of acetylene from polymer-grade ethylene, is a commercially important process. The process uses supported Pd catalysts (Boitiaux, et al., 1985), which contain various promoters (Leviness, et al., 1984; Zhang, et al., 2000; Shin, et al., 2002; Kang, et al., 2002) for improving the ethylene selectivity and the catalyst lifetime. However, the catalysts should be further improved because they require a narrow range of reaction condition to achieve a high ethylene selectivity and their lifetime is relatively short, commonly less than a year.

In this study, we added La and Nb oxides to Pd/SiO₂ as potential promoters for improving the ethylene selectivity and lifetime. This attempt originated from the work by Tauster and Fung (Tauster and Fung, 1978) who reported that metal particles...
supported on transition-metal oxides interacted strongly with the support, so-called a strong metal-support interaction (SMSI). We prepared Pd/SiO₂, Pd-La/SiO₂, and Pd-Nb/SiO₂, reduced them at different temperatures, and compared their performance in acetylene hydrogenation. Deactivation tests under severe reaction conditions allowed us to compare the catalyst aging behaviors.

The catalyst surface was analyzed by H₂ chemisorption, X-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption (TPD). Thermogravimetric analysis (TGA) and temperature-programmed oxidation (TPO) were used to study the coke accumulated on the deactivated catalyst surface.

**EXPERIMENTS**

1wt% Pd/SiO₂ was prepared as a reference catalyst by an ion-exchange method using silica support (D11-10 obtained from BASF, surface area=184 m²/g) and Pd(NH₃)₄(OH)₂ as a Pd precursor following a procedure in literature (Liotta, et al., 1996). La- and Nb-modified Pd catalysts were prepared by impregnating 1wt% Pd/SiO₂ with an aqueous solution of La(NO₃)₃·xH₂O and a hexane solution of tetrakis(2,2,6,6-tetramethyl-3,5-heptanedio-nato)niobium, Nb(C₁₁H₁₉O₂)₂, respectively, followed by calcination at 300°C for 2 hours. The amounts of La, Nb, and Pd contained in the catalysts were analyzed by ICP-AES (Shimadzu/ICPS-1000). The atomic ratio of La to Pd or Nb to Pd was adjusted to 1.0.

Acetylene hydrogenation was performed in a pyrex micro-reactor at atmospheric pressure using an ethylene stream containing 1.02% acetylene as a feed at different temperatures. The H₂/acetylene ratio in the reaction stream was 2, and the flow rate of reactant mixture was varied from 20 to 120ml/min, i.e., space time from 1.52×10⁻³ min to 2.53×10⁻⁴ min, to change the acetylene conversion. The reaction condition for deactivation tests were more severe than those in selectivity measurements so that catalysts were deactivated at higher rates. That is, the reaction temperature was 90°C, the reactant stream contained 4.1% acetylene in ethylene, and the H₂/acetylene ratio in the reaction stream was 1. Reaction products were analyzed with an on-line G.C. (Agilent, model 6890 series with FID) using a capillary column.

Hydrogen uptake by the sample catalysts was measured at 35°C with ASAP 2010 (Micrometrics Co.). Prior to the measurements, the sample was reduced and the amounts of hydrogen chemisorbed on the sample surface were determined using the back-sorption method (Benson, et al., 1973). The chemical properties of the catalyst surface were examined with XPS (VG ESCA LAB-5) equipped with an Al Kα anode. For ethylene TPD experiments, a catalyst sample, which had been pre-reduced and exposed to a mixture of ethylene and helium, was heated from room temperature to 300°C at a rate of 10°C/min in a flowing helium gas, while the effluent gas was analyzed with a mass spectrometer (VG Sensorlab).

Catalysts used for the same accumulated conversion of acetylene were analyzed thermogravimetrically (TA Instruments, TGA 2050) in air flowing at 40ml/min. The temperature was raised from 30°C to 850°C at a rate of 10°C/min. The TPO experiment was conducted by raising temperature from 30°C to 800°C at a rate of 10°C/min in flowing 100% O₂. The effluent gas was analyzed by a mass spectrometer.
RESULTS AND DISCUSSION

Acetylene Hydrogenation

Figure 1 compares the ethylene selectivity of Pd/SiO₂, Pd-La/SiO₂ and Pd-Nb/SiO₂ obtained by reaction at 60℃. The ethylene selectivity of Pd/SiO₂ is lowered after reduction at 500℃ (Pd/500) due to the sintering of Pd particles, but Pd-La/SiO₂ and Pd-Nb/SiO₂ showed the selectivity higher than that of Pd/300 after reduction at 300℃ or 500℃, particularly in the case of Pd-La/SiO₂ reduced at 500℃ (Pd-La/500). Figure 2 shows the ethylene selectivities of Pd/SiO₂ and Pd-Nb/SiO₂ obtained at 50℃. Although the conversion is decreased from one obtained at 60℃, the selectivity of Pd-Nb/SiO₂ is much improved after reduction at 300℃, 400℃ or 500℃. As a result, the promotional effect of Nb oxide is larger at 50℃ than 60℃.

![Figure 1. Ethylene selectivity versus conversion on various catalysts (Reaction Temp.=60℃)](image1)

![Figure 2. Ethylene selectivity versus conversion on various catalysts (Reaction Temp.=50℃)](image2)

It is noteworthy in Figures 1 and 2 that the acetylene conversion is increased by Nb oxide addition. This beneficial effect comes from the additional hydrogenation activity of Nb oxide (Moyes, et al., 2002), as confirmed by our separate reaction experiments using Nb oxide for acetylene hydrogenation.

Deactivation

We have plotted the acetylene conversion normalized to the initial value versus the accumulated amount of converted acetylene, such that the deactivation behaviors of different catalysts are compared based on the same load of the reaction.

In Figure 3, the deactivation rate of Pd/300 is higher than those of catalysts modified with La and Nb oxides, which indicates that the catalyst deactivation is retarded on the La- and Nb-modified catalysts.
H\textsubscript{2}-Chemisorption

Table 1 lists the amounts of H\textsubscript{2} irreversibly adsorbed on the catalysts after reduction at different temperatures, 300\textdegree C and 500\textdegree C. On Pd only catalyst, the H\textsubscript{2} uptake is decreased when the reduction temperature is raised from 300\textdegree C to 500\textdegree C, which is due to the sintering of Pd particles as confirmed by separate IR observations of CO adsorbed on the catalysts. Pd-La/500 and Pd-Nb/500 also exhibit decreases in the amounts of chemisorbed H\textsubscript{2} because the Pd surface is partially covered with the oxides. This remarkable decrease in the H\textsubscript{2} uptake after reduction at 500\textdegree C is a typical result of the SMSI phenomenon.

Table 1. H\textsubscript{2}-Chemisorption

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H/Pd</th>
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<tbody>
<tr>
<td>Pd/300</td>
<td>0.45</td>
</tr>
<tr>
<td>Pd/500</td>
<td>0.37</td>
</tr>
<tr>
<td>Pd-La/300</td>
<td>0.24</td>
</tr>
<tr>
<td>Pd-La/500</td>
<td>0.16</td>
</tr>
<tr>
<td>Pd-Nb/500</td>
<td>0.22</td>
</tr>
<tr>
<td>Pd-Nb/500</td>
<td>0.17</td>
</tr>
</tbody>
</table>

XPS

In Figure 4, the XPS peak at 336.1 eV, observed on Pd/300, is shifted to lower energies, by about 0.5 eV, on Pd-La/500 and Pd-Nb/500. According to Fleisch et al. (Fleisch, et al., 1984), this peak shift is originated from the metal-support interaction. The peak is shifted to lower energies because metal oxides, which become rich in electron density after the partial reduction at 500\textdegree C, donate electrons to the Pd surface.
Ethylene-TPD

The peaks of ethylene-TPD from Pd surface appear at different temperature ranges depending on the characteristic modes of ethylene adsorbed on the surface. In Figure 5, Pd/300 shows three major peaks of ethylene, which are assigned as follows based on the analysis by Stuve and Madix (Stuve and Madix, 1985). Peak I is assigned to π-bonded ethylene, Peak II is originated from di-σ-bonded ethylene, and Peak III is due to the triply-bound species, ethylidyne. The TPD peaks change in two ways on modified catalysts: the suppression of peak intensity and the shift of Peak I to lower temperatures.

The suppression of Peak II and III indicates that the multiply-coordinated sites of the Pd surface decrease with oxide addition. This is possible when metal oxides spread on and block the Pd surface by decoration effect. The shift of Peak I to lower temperatures indicates that the ethylene adsorption is weakened by the oxide addition, which occurs when electrons are transferred from the oxide to the Pd surface. This explanation agrees with the XPS result.
TGA and TPO

To clarify the coke composition and the effect of coke on the catalyst performance, TGA and TPO were conducted using deactivated Pd/300 and Pd-La/500 as sample catalysts. TGA curves in Figure 6 deviate from each other at temperatures above 250°C, which occurs largely due to the difference in the burn-off amounts of green oil deposited on the catalysts. At the final temperature of 800°C, Pd/300 lost the initial weight by about 58.9% while Pd-La/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 Figure 7. Three major peaks are observed in different temperature regions: below 300°C, 300°C-500°C, and above 500°C. According to Larsson et al. (Larsson, et al., 1998), who obtained results similar to this study in their analysis of coke by TPO, the peak below 300°C, designated as Peak I in Figure 7, is due to heavy hydrocarbons that are adsorbed on the catalyst surface or adsorbed in the catalyst pores. Peak II, observed between 300°C and 500°C, represents coke on or in the vicinity of Pd, and Peak III above 500°C indicates coke produced on the support without the influence of Pd. Two changes are notable in Figure 7 as a result of the promoter modification: 1) characteristic changes in the intensity of three major peaks, and 2) peak shift to lower temperatures, which is particularly large with Peak III. The intensity of Peak II was significantly decreased due to the La-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 the La-added catalyst.

Figure 6. TGA results on Pd/300 and Pd-La/500

To estimate the amounts of coke and compare the characteristics of coke deposited on different catalysts, TPO was additionally performed. Mass spectrometer was used to monitor CO₂ because coke on the catalysts reacted with O₂ to produce CO₂ and CO. Figure 8 shows the profiles of CO₂ and CO obtained by the TPO experiments. Modified Pd/SiO₂ produces less amounts of CO₂ and CO compared
with the case of Pd/SiO₂. Furthermore CO₂ and CO are produced at lower temperatures on modified Pd/SiO₂ than on Pd/SiO₂. These results are in accordance with the above DTGA results indicating that coke is produced in less amounts and more volatile on modified Pd/SiO₂ than on Pd/SiO₂.

CONCLUSIONS

The ethylene selectivity and deactivation behavior of Pd/SiO₂ in acetylene hydrogenation are significantly improved after reduction at 500°C when the catalyst surface is modified with La and Nb oxides. This is because the Pd surface is covered with small patches of partially reduced La and Nb oxides and is also electronically modified by a phenomenon similar to the SMSI.

ACKNOWLEDGMENTS

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