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Properties of Si-modified Pd catalyst for selective hydrogenation of acetylene

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Abstract

Supported Pd catalysts have been modified with Si deposited on them by silane decomposition. When used in acetylene hydrogenation, the Si-modified catalysts show higher selectivity for ethylene and produce less amount of green oil than the unmodified Pd catalysts. IR and XPS analyses of the catalysts suggest that Si covers the Pd surface as Si or SiO_2 patches. The Pd surface is diluted with the deposited Si as observed by IR spectra of CO adsorbed on the surface. However, the electronic property of the Pd surface seems to be unaffected by the Si species because such a modification is not observed in XPS nor acetylene-TPD analysis. Accordingly, we conclude that improved performance of the Si-modified catalysts comes mostly from geometric modification of the Pd surface by Si.

1. Introduction

Ethylene stream in the naphtha craking unit contains a small quantity of acetylene which is a poison in the ensuing process of ethylene polymerization. Selective hydrogenation is a method to remove acetylene in the stream, and supported Pd catalysts are commonly used for the reaction. Two factors are important in the process. One is the ethylene selectivity, i.e. fraction of ethylene produced by acetylene conversion, and the other is the catalyst lifetime which is limited by green-oil deposition during reaction.

Various promoters such as Ag, Cr, Cu, Co and alkali metals have been added to the catalysts to improve their performance [1–5]. Role of the promoters is considered in two aspects: geometric and electronic effects. Geometric modification is considered because the promoter atoms located on the Pd surface decrease the amounts of the multiple Pd sites responsible for the selectivity deterioration [3]. The promoter also modifies the Pd surface electronically to alter the adsorption strength between Pd and the adsorbates.

In this study, we have deposited Si on supported Pd catalysts by CVD method and evaluated them for selective hydrogenation of acetylene. The catalyst surface has been analyzed by CO chemisorption, FT–IR, acetylene-TPD and XPS to understand the nature of the Si modification.

2. Experimental

2.1. Catalyst preparation

1 wt.% Pd/SiO_2 and 2 wt.% $Pd/\alpha\text{-}Al_2O_3$ were prepared as model catalysts. 1 wt.% Pd/SiO_2 was prepared by incipient wetness impregnation using $Pd(NO_3)_2\cdot x(H_2O)$ as a precursor. SiO_2 was obtained from the Catalysis Society of Japan (JRC-SIO-6,

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Surface area=109 m^2/g). 2 wt.% Pd/α-Al_2O_3 was prepared by wet impregnation with an acetone solution of palladium acetylacetonate (Aldrich). α-alumina was obtained from Showa Denko (surface area=4.36 m^2/g). 1 wt.% Pd/SiO_2 was dried in an air-circulating oven at 100°C for 12 h, and 2 wt.% Pd/α-Al_2O_3 in a vacuum oven at 40°C for 4 h. Both catalysts were calcined in air at 300°C for 4 h and reduced in H_2 at 300°C for 1 h before use in reaction.

Si deposition was carried out by CVD method in an atmospheric apparatus, which is shown in Fig. 1. SiH_4 was used as a precursor for Si deposition. After in-situ reduction of the catalyst, 1% SiH_4/H_2 mixture was injected as pulses into H_2 stream flowing to a CVD reactor maintained at 250°C. The amount of added SiH_4 was controlled by the number of the repetitive injections. After Si deposition, the catalyst was cooled to room temperature, then exposed to O_2 for 2 h.

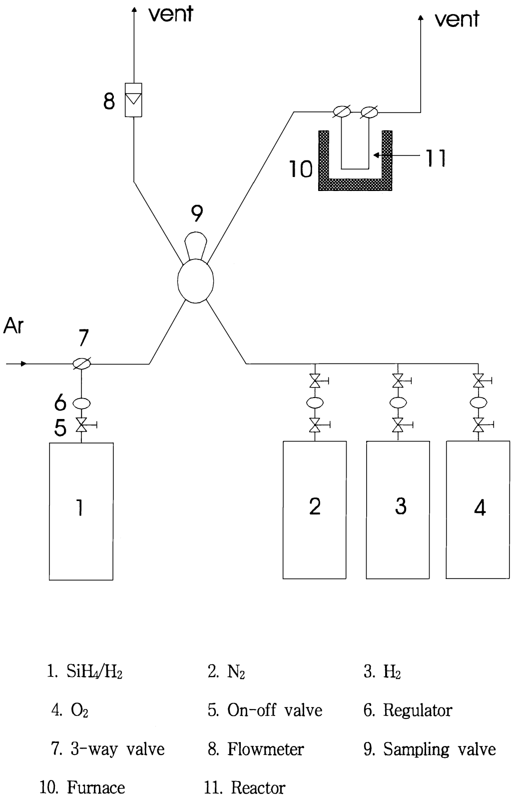


Fig. 1. Schematic diagram of CVD apparatus.

2.2. Chemisorption and FT-IR

Chemisorption was carried out in a static volumetric unit using CO as a probing gas. CO isotherms were obtained in the pressure range of 30–150 Torr. IR spectra of CO adsorbed on the catalysts were recorded with a spectrometer (Midac, model 2100) in an IR cell with KBr windows [6]. The sample catalyst was pressed into a self-supporting disc, placed in the cell, reduced at 300°C, and exposed to 10 Torr of CO. IR spectra of adsorbed CO were recorded after removing gaseous CO by evacuation.

2.3. TPD, TPO and XPS

Temperature-programmed desorption (TPD) of acetylene from the catalyst was performed after exposing the catalyst to acetylene/He mixture at room temperature. He was used as a carrier gas and heating rate was 20°C/min. Temperature-programmed oxidation (TPO) of carbonaceous species on the used catalyst was made in the same manner as TPD. The sample was heated in O_2 at 10°C/min. The effluent gases were monitored with a mass spectrometer (VG, Sensorlab 200). The surface of the modified catalysts was analyzed with XPS (Perkin–Elmer, PHI-558) equipped with Mg K_α (1253.6 eV) anode. After reduction at 300°C and exposure to O_2 at room temperature, the catalyst was protected from air oxidation by wetting the surface with iso-octane, mounted on a double-sided adhesive tape, then placed in a UHV chamber for analysis. All XPS data were corrected with C 1s peak (284.6 eV).

2.4. Catalytic test

Acetylene hydrogenation was performed in a pyrex micro-reactor. Gas mixture containing 0.61% acetylene in ethylene prepared by the Korea Research Institute of Standard and Science, was used for the reaction. Reaction products were analyzed with an on-line G.C. (Gow-Mac, model 750 with FID) using Porapak N as a column material. The flow rate of the reactant mixture was varied between 40 and 120 ml/min to change the acetylene conversion.

3. Results and discussion

3.1. Si deposition on Pd

Fig. 2 shows peaks of silane detected by mass spectroscopy in an outlet of a CVD reactor containing 0.1 g of catalyst sample when pulses of silane diluted to 1% in H_2 are injected repetitively to the reactor. When the reactor contains SiO_2, silane peaks are detected readily after injecting 0.25 ml of the silane mixture. On the other hand, when the reactor contains Pd/SiO_2, the peak appears after 11 ml of the silane mixture has been injected to the reactor. The result indicates that SiO_2 is almost inactive but Pd/SiO_2 is active for silane decomposition. We have repeated the experiments with Al_2O_3 and Pd/Al_2O_3 to confirm the same trend.

Table 1 lists the amounts of Si deposited on 0.1 g of each sample, estimated assuming that all Si produced by silane decomposition is deposited on the sample. The amount of Si is larger on Pd/Al_2O_3 than on Pd/SiO_2 because the former contains more Pd. Similar results as in this study have been reported previously [7] for decomposition of triethylsilane of Pd.

Table 2 lists two modified Pd/SiO_2 catalysts of different Si contents obtained by decomposing different amounts of silane in the CVD reactor. The catalysts adsorb different amounts of CO depending on the Si contents. This may occur, when either the catalyst pores are blocked by or the Pd surface is covered with Si. Pore blocking by Si is not likely because the pore size distribution of the catalyst is unaffected by the Si deposition. Accordingly, the Pd surface is partially covered with Si which inhibits CO chemisorption on the surface. Again, this tendency is consistent with a previous report [7].

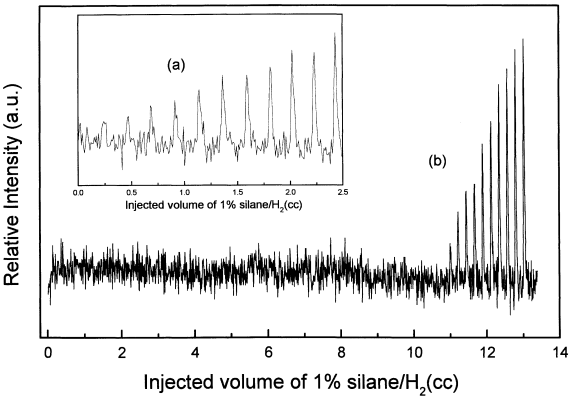


Fig. 2. Silane peaks detected in the outlet of a CVD reactor after repetitive injections of silane mixture. (a) SiO_2 (b) Pd/SiO_2.

Table 1
Amounts of silane consumed in a CVD reactor containing 0.1 g of different samples

Sample	Alumina	Silica	1 wt.% Pd/SiO_2	2 wt.% Pd/Al_2O_3
Silane consumption (10^{-7} mol)	3.1	1.2	46.8	80.3

Table 2
The amounts and modes of CO adsorption on 0.1 g of different catalysts

Catalysts	Amount of deposited Si (10^{-7} mol)	Si/Pd	CO/Pd	A_{cb}/A_{ib} [b]
Pd/SiO_2	0	0	0.1	1.1
CVD2[a]	8.9	0.095	0.067	0.36
CVD4[a]	17.8	0.19	0.027	0

[a] CVDX represents a Si-modified catalyst. X indicates volume (ml) of 1% silane/H_2 mixture injected to H_2 stream flowing to a CVD reactor containing 0.1 g of Pd/SiO_2.

[b] Intensity of compressed-bridged band (A_{cb})/Intensity of isolated-bridged band (A_{ib}).

3.2. IR spectra of adsorbed CO

Fig. 3 compares IR spectra of CO adsorbed on Pd/SiO_2, CVD2, and CVD4. The spectra observed in this study are similar to those reported previously [8,9]. The overall spectral intensity decreases with Si deposition, in agreement with the CO-chemisorption results. CO adsorbs on Pd in four modes [10]: linear, compressed-bridged, isolated-bridged, and tri-coordinated bonds. Table 3 describes the adsorption modes and their peak locations.

A notable feature in Fig. 3 is that the intensity of a sharp band at 1995 cm^{-1}, assigned to the compressed-bridged CO bond, decreases rapidly with Si deposition. The intensity ratios of the compressed- to the isolated-bridged CO bands are given in Table 2. The intensity change is explained as follows. The compressed-bridged mode of CO adsorption needs three

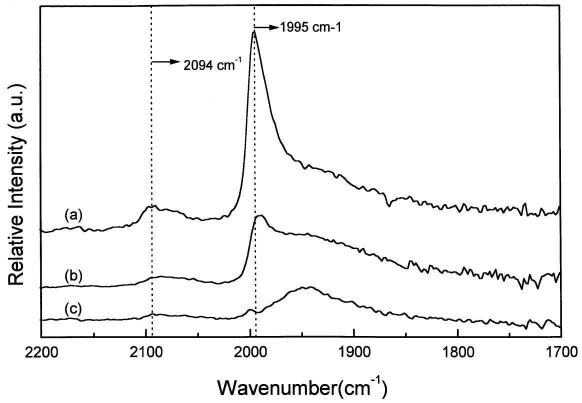
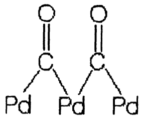
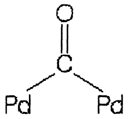
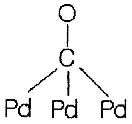


Fig. 3. IR spectra of CO adsorbed on various catalysts. (a) Pd/SiO_2 (b) CVD2, (c) CVD4.

Table 3
Assignment of IR bands of CO adsorbed of Pd [10]

Band	Wavenumber (cm^{-1})	Species
Linear	2100–2050	
Compressed-bridged	1995–1975	
Isolated-bridged	1960–1925	
Tri-coordinated	1890–1870	

adjacent Pd atoms, but the isolated-bridged mode needs only two. When Si is deposited on the Pd surface, it is likely that the sites requiring three adjacent Pd atoms are blocked more rapidly than the sites requiring two atoms. Accordingly, the IR provides an evidence that the surface ensembles comprising many Pd atoms are inhibited by Si deposition.

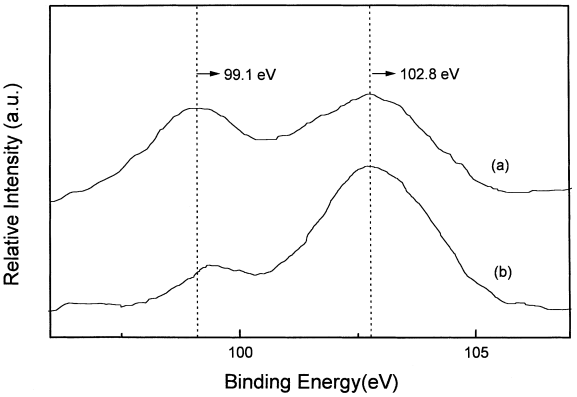


Fig. 4. XPS of Si 2p on various catalysts. (a) CVD5, (b) CVD10 (both are Si-modified Pd/Al_2O_3).

3.3. XPS and acetylene-TPD

XPS of Si 2p on the Si-modified catalysts are presented in Fig. 4. The spectra corrected with carbon 1s show two major peaks at 99.1 and 102.8 eV, which are assigned to Si and SiO_2, respectively. Accordingly, a fraction of the deposited Si remains unoxidized, possibly interacting with Pd, after the oxidation step. We therefore conclude that, the Pd surface is partially covered with Si and SiO_2 patches. Smith et al. [7,11] have suggested that Si forms an alloy with Pd.

Fig. 5 shows XPS of Pd $3d_{5/2}$ on the modified catalysts. The binding energy of metallic Pd $3d_{5/2}$ is 334.9 eV [12]. When Si interacts with Pd, the binding

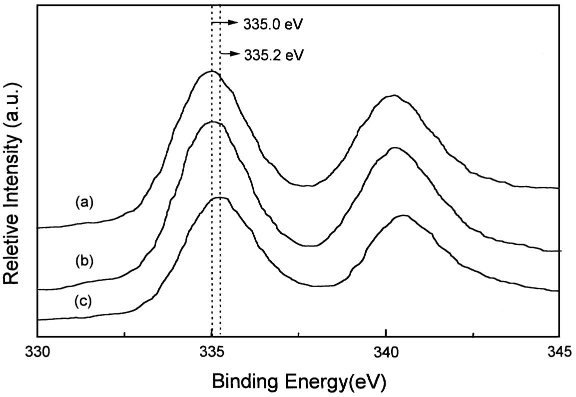


Fig. 5. XPS of Pd 3d on various catalysts. (a) Pd/Al_2O_3, (b) CVD5, (c) CVD10 (All are Si-modified Pd/Al_2O_3).

energy changes due to charge transfer or relaxation energy [13,14]. Grunthaner et al. [15] showed that binding energy of Pd $3d_{5/2}$ increased by 1.6 eV when Pd–Si alloy was formed in the Pd–Si interface. The formation of Pd–Si alloy in supported catalysts also increased the binding energy by 1–1.5 eV [16].

Fig. 5 shows that the binding energy on Pd/SiO_2, CVD2 and CVD4 is 335.0, 335.0 and 335.2 eV, respectively. The energy difference among the catalysts, 0.2 eV, is smaller than one reported by others [15,16]. Riley et al. [13] have proposed that a small increase of Pd $3d_{5/2}$ binding energy in amorphous $Pd_{0.81}Si_{0.19}$ system is not due to charge transfer from Pd to Si, but due to relaxation energy. We believe that the binding energy difference in this study is also due to relaxation energy and that the initial electronic state of Pd is not changed by the Si deposition. Pd–Si alloy suggested by Smith et al. [7,11] is not observed in this study.

TPD of acetylene adsorbed on Pd/SiO_2 gives a single peak at 150°C, and the peak location is the same on the Si-modified catalysts (Fig. 6). Accordingly, a new adsorption site for acetylene is not produced nor the electronic state of Pd is changed by the Si deposition. The result agrees with the XPS results, which also indicates that the Si species does not modify Pd electronically.

3.4. Catalytic performance of Si-modified catalysts

Performance of the Si-modified catalysts in acetylene hydrogenation has been compared with one of the unmodified Pd/SiO_2 and Pd/Al_2O_3 as shown in Figs. 7 and 8. The ethylene selectivity has been obtained over a range of conversion because the former depends on the latter. Obviously, the ethylene selectivity is improved when the catalysts are modified with Si. The selectivity improvement increases the ethylene yield in acetylene hydrogenation and also allows use of the catalysts at high H_2/acetylene ratios, which extends the catalyst lifetime.

To compare the extents of catalyst deactivation by green oil accumulation, we have analyzed the catalysts

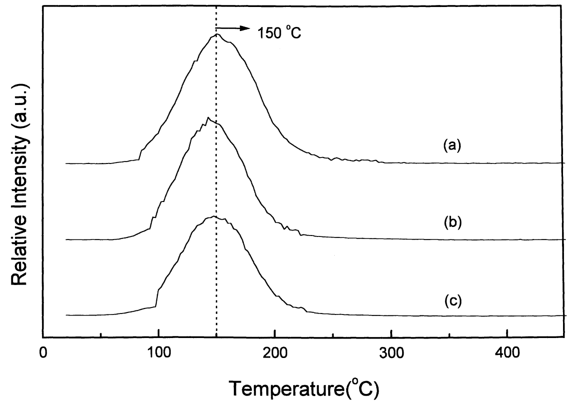


Fig. 6. Acetylene-TPD from various catalysts. (a) Pd/SiO_2, (b) CVD2, (c) CVD4.

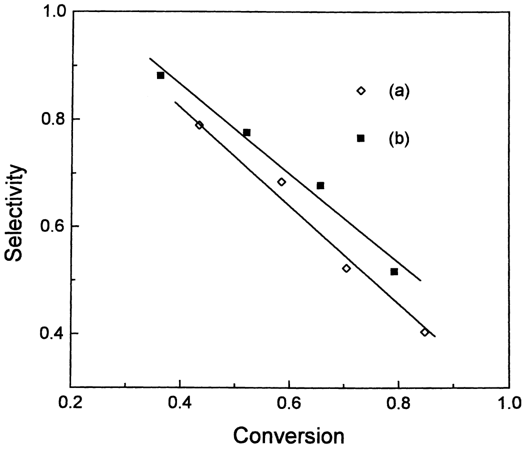


Fig. 7. Ethylene selectivity vs. conversion in acetylene hydrogenation. (H_2/acetylene=2, T=60°C) (a) Pd/SiO_2, (b) CVD2.

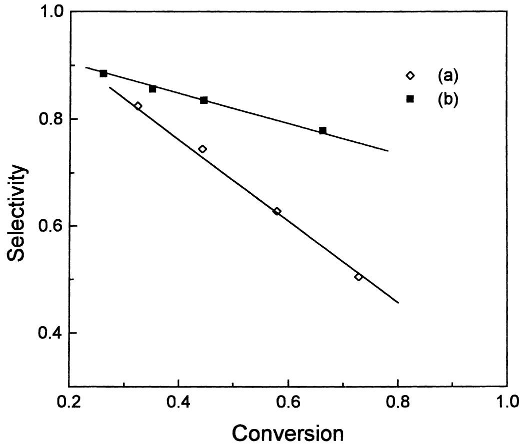


Fig. 8. Ethylene selectivity vs. conversion in acetylene hydrogenation. (H_2/acetylene=3, T=100°C) (a) Pd/Al_2O_3, (b) CVD5 (Si-modified Pd/Al_2O_3).

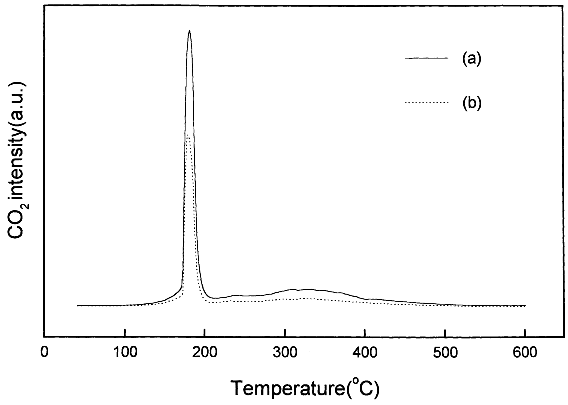


Fig. 9. TPO of the surface species on catalysts used for the same load of conversion. (a) Pd/SiO_2, (b) CVD2.

for carbon contents after they have been used under the same load of conversion. Fig. 9 shows two TPO peaks obtained from the used catalysts. CO_2 peaks observed at different locations represent coke adsorbed on Pd atoms of different coordinations [17]. The total area of the peaks on CVD2 is smaller than on Pd/SiO_2, indicating that the formation of green oil on the catalyst is suppressed by Si modification.

3.5. *Role of Si*

Many studies have been reported previously [3,18] about the mechanism of acetylene hydrogenation to produce either ethylene or ethane. The reaction proceeds via two paths. Path I is hydrogenation of acetylene to ethylene on the Pd surface followed by desorption of ethylene to gaseous product or further hydrogenation of ethylene to ethane. Path II is hydrogenation of adsorbed acetylene of intermediate species such as ethylidyne or ethylidene, which is not hydrogenated to ethylene but directly to ethane.

Obviously, Path I contributes to ethylene production and Path II lowers the ethylene selectivity. Even in Path I, the extent of hydrogenation should be regulated for maximum selectivity because ethylene and ethane are produced in sequence. In path II, the Pd surface with multiple adsorption sites is essential because the intermediate species, ethylidyne or ethylidene, is bound to three or two Pd atoms.

Many attempts have been made to develop catalysts of improved ethylene selectivity [2–5,19]. One approach is to prepare catalysts of high metal dispersions [19]. Small Pd particles in highly dispersed catalysts allow few Pd planar sites, i.e. multiple adsorption sites, which results in suppression of the ethylidyne or ethylidene species in Path II. Small Pd particles also accommodate less amount of β-Pd hydride than large particles. Since, the β-Pd hydride is responsible for non-selective hydrogenation of acetylene, small Pd particles are beneficial to improved selectivity.

Another approach to improve the selectivity is to add a second metal to the catalyst, so that the added metal either forms an alloy with Pd or modify the Pd surface [1–5,20]. β-Pd hydride is suppressed on many Pd alloys [3]. Additionally, proper dilution of the Pd surface with a second metal will inhibit formation of the ethylidyne or ethylidene species in Path II. A second metal sometimes modifies the Pd surface electronically, so that its adsorption strength for acetylene and ethylene is altered [2,4,5,20].

Improved selectivity of the Si-modified catalyst in this study may be explained as follows, based on our experimental results and the above reaction mechanism. Deposited Si and SiO_2 dilute the Pd surface, as confirmed by our CO chemisorption and IR results, which suppresses adsorption of ethylidyne and ethylidene species in Path II. Pd–Si alloy is not observed in our XPS analysis, yet a possibility remains that the surface Si species retard the formation of β-Pd hydride. Si does not seem to modify the Pd surface electronically unlike the cases of other promoter metals.

Suppression of green oil formation on the Si-modified catalyst is also explained by the dilution effect of the deposited Si species. Polymerization to yield green oil will obviously be retarded when the Pd surface is geometrically blocked by inactive Si species.

4. Conclusions

Si-modified Pd catalysts prepared by deposition of Si on them by silane decomposition show the following surface and catalytic properties.

1. Pd catalyzes silane decomposition and most of the decomposed Si is deposited selectively on the Pd surface.

2. The modified Pd surface is composed of Pd, Si and SiO_2. The Si species modify the Pd surface geometrically but not electronically.
3. Si-modified catalysts have higher ethylene selectivity and longer catalyst lifetime than monometallic Pd catalysts in selective hydrogenation of acetylene.
4. Improved performance of the modified catalysts is due to geometric modification of the Pd surface with Si, which reduces the multiple adsorption sites for undesirable reaction intermediates, and possibly due to suppression of β-Pd hydride on the catalyst.

Acknowledgements

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