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Selective hydrogenation of acetylene on Pd/SiO_2 catalysts promoted with Ti, Nb and Ce oxides

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Abstract

Transition-metal oxides added to Pd/SiO_2 improve significantly the activity and the ethylene selectivity of the catalyst in acetylene hydrogenation, which is caused by the interaction between the oxides and the Pd surface similar to the case of the oxide-supported catalysts. It has been confirmed through experiments that metal oxides spread on and modify both geometrically and electronically the Pd surface after the catalyst is reduced at 500°C. Such a behavior of metal oxides in the catalyst is correlated well with their promotional effect on the catalyst performance. That is, the oxides on the Pd surface retard the sintering of the dispersed Pd particles, suppress the adsorption of ethylene in the multiply-bound mode, and facilitate the desorption of ethylene produced by acetylene hydrogenation. Among the three metal oxides examined in this study, Ti oxide is found to have the most promotional effect. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Palladium catalyst; Transition-metal oxide; Acetylene hydrogenation; Promoter

1. Introduction

Ethylene stream from the overhead of a deethanizer unit in naphtha cracker contains about 0.1–1% of acetylene as an impurity, which should be lowered to below 5 ppmv so that the ethylene stream may be used as a feed for the next polymerization process. Two methods are used to lower the acetylene level. One is separation from ethylene through adsorption, for example with zeolite, and the other is conversion to ethylene by selective hydrogenation using Pd catalysts [1].

Although various components such as Ag [2], Ni [3], Cu [4], K [5], and Si [6] have been proposed as promoters of the Pd catalysts, the catalysts still need improvements in their lifetime and ethylene selectivity [7]. In this study, we have used Ti, Nb and Ce oxides as promoters of the Pd catalyst. This attempt originated from the work by Tauster et al. [8,9] who reported that metal particles supported on transition-metal oxides interacted strongly with the support, so-called a strong metal–support interaction (SMSI), when the catalysts were reduced at high temperatures, such as 500°C. The catalysts exhibited a significant suppression in H_2 chemisorption and yielded unique kinetic results in CO hydrogenation [10–13] and other reactions [14] after the high-temperature reduction.

However, most of the previous works on SMSI phenomenon were made with catalysts prepared using transition-metal oxides as supports. In this study, we have examined the oxides as promoters of the Pd catalyst, instead of supports, for acetylene hydrogenation. Pd/SiO_2 catalysts promoted with TiO_2, Nb_2O_5, or CeO_2 have been prepared, reduced at different temperatures, and their performance in acetylene hydrogenation observed. We analyzed the catalyst surface by CO chemisorption, IR spectroscopy of adsorbed

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CO, XPS, and ethylene-TPD to understand the nature of the metal–oxide interaction.

2. Experimental

2.1. Catalyst preparation

1 wt.% Pd/SiO_2 was prepared by ion-exchange method using $Pd(NH_3)_4(OH)_2$ as a Pd precursor. Silica (Aerosil Degussa, 200 m^2/g) was added to a solution of $Pd(NH_3)_4(OH)_2$ and the suspension was stirred for 2 h before centrifuging. The catalyst cake was washed in water, dried at 110°C overnight, and calcined in air at 300°C for 2 h.

Pd catalysts modified with transition-metal oxides, designated as $Pd–X/SiO_2$ (X = Ti, Nb, Ce), were prepared by impregnating 1 wt.% Pd/SiO_2 with a hexane solution of $Ti(OC_3H_6)_2(C_{11}H_{19}O_2)_2$, $Nb(C_{11}H_{19}O_2)_2$, and $Ce(C_{11}H_{19}O_2)_2$, respectively. The atomic ratio of X/Pd was adjusted to 1. The catalyst samples were then calcined in air at 300°C for 3 h and reduced in H_2 at either 300 or 500°C for 1 h before use in the reaction.

2.2. CO chemisorption and FT-IR

The amounts of CO chemisorbed on the catalysts were measured at room temperature in a conventional glass vacuum system. The CO pressure for adsorption ranged between 30 and 150 Torr. For the IR observation, the sample catalyst was pressed into a self-supporting wafer, placed in the IR cell [15], reduced either at 300 or 500°C, and then exposed to 40 Torr of CO. Midac 2100 was used for the IR measurements.

2.3. XPS and TPD

The X-ray photoelectron spectra (XPS) of the catalyst surface were obtained with VG ESCA LAB-5, and the binding energy was corrected by taking C_{1s} line at 284.6 eV as an internal standard.

For the ethylene-TPD experiments, the reduced catalyst was exposed to a mixture of ethylene and helium, then flushed with pure helium at room temperature to remove weakly adsorbed ethylene species. The TPD was performed by heating the sample at the rate of 10°C/min in a 20 cm^3/min flow of helium. The effluent gas was analyzed with a mass spectrometer (VG Sensorlab).

2.4. Acetylene hydrogenation

A gas mixture containing 0.91% acetylene in ethylene was flowed through a Pyrex micro-reactor at 40°C. The acetylene conversion was adjusted by changing the reactant flow rate between 40 and 120 ml/min, and the products were analyzed with an on-line gas chromatograph (HP Model 5890 with FID) using a Porapak N column.

3. Results and discussion

3.1. Acetylene hydrogenation

Table 1 compares the conversions obtained with different catalysts under the identical reaction conditions. After reduction at 300°C, Pd/SiO_2 shows slightly higher conversion than $Pd–X/SiO_2$ catalysts. We believe that this is because the Pd surface is partially covered with metal oxides on the modified catalysts. When the catalysts are reduced at 500°C, the conversion on Pd/SiO_2 decreases significantly apparently due to the sintering of Pd particles during the high-temperature reduction. The conversions on $Pd–X/SiO_2$ are also lowered but the extent is not so great as in the case of Pd/SiO_2. Accordingly, it seems that the sintering of Pd particles is retarded on $Pd–X/SiO_2$ due to the addition of metal oxides.

Table 1
Acetylene conversions on various catalysts reduced at 300 or 500°C[a]

	Reduction temperature (°C)	Conversion
Pd/SiO_2	300	0.89
	500	0.68
$Pd–Ti/SiO_2$	300	0.85
	500	0.75
$Pd–Nb/SiO_2$	300	0.83
	500	0.73
$Pd–Ce/SiO_2$	300	0.81
	500	0.72

[a] Reaction conditions: temperature = 40°C; H_2/acetylene = 2; SV = 3000/min.

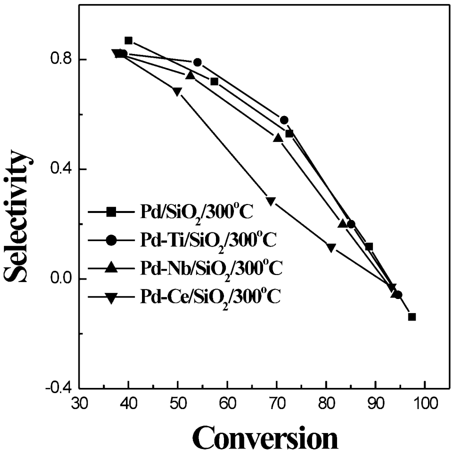

Fig. 1. Reaction results on various catalysts after reduction at 300°C.

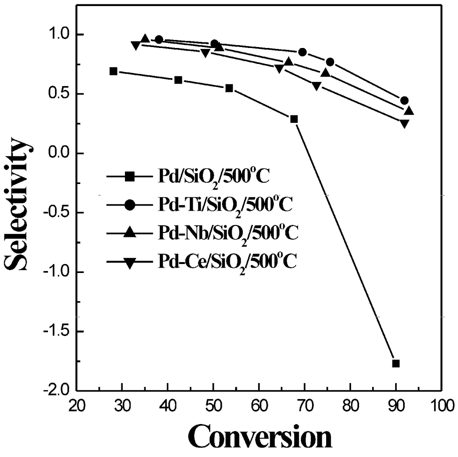

Fig. 2. Reaction results on various catalysts after reduction at 500°C.

Fig. 1 shows changes in the ethylene selectivity with the conversion for the catalysts reduced at 300°C. Since ethylene is produced as an intermediate in the consecutive hydrogenation process, the ethylene selectivity decreases with the acetylene conversion. The ethylene selectivity is relatively high on Pd/SiO_2 and Pd–Ti/SiO_2 while it is low on Pd–Ce/SiO_2. Therefore, the addition of metal oxides to Pd/SiO_2 is not so beneficial to the selectivity improvement when the catalysts are reduced at 300°C.

However, the selectivity is significantly improved when Pd–X/SiO_2 catalysts are reduced at 500°C. Fig. 2 indicates that the oxide-modified catalysts show high selectivity over a wide range of conversions while Pd/SiO_2 shows low values. Negative selectivity indicates a net ethylene loss in the process. The selectivity on Pd–X/SiO_2 is even higher than on Pd/SiO_2 reduced at 300°C, and increases in the following order: $\mathrm{Pd{-}Ce/SiO_2} < \mathrm{Pd{-}Nb/SiO_2} < \mathrm{Pd{-}Ti/SiO_2}$.

The ethylene selectivity degrades in the case of Pd/SiO_2 because Pd particles are sintered, accordingly to have more low-index Pd surface, in the reduction step [16]. Although Pd–X/SiO_2 catalysts are also sintered after reduction at 500°C, the extent seems to be small as indicated by the conversion data in Table 1. Therefore, the selectivity improvement is partly due to the retardation of the sintering on Pd–X/SiO_2. However, the fact that the selectivity on Pd–X/SiO_2 reduced at 500°C is even higher than on Pd/SiO_2 reduced at 300°C suggests that an additional factor is involved in the selectivity improvement.

3.2. CO chemisorption and IR observation

Fig. 3 compares the IR spectra of CO adsorbed on the catalysts reduced at either 300 or 500°C, and Table 2 lists the amounts of CO chemisorption and the area ratios of the IR bands representing the multiply- and the linearly-bound CO, A_m/A_l. The IR bands of CO adsorbed on Pd are divided into four modes depending on their locations: linear (2100–2200 cm^{-1}), compressed-bridged

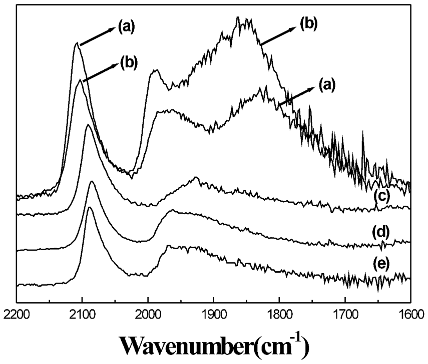

Fig. 3. IR spectra of CO adsorbed on various catalysts: (a) Pd/SiO_2/300°C; (b) Pd/SiO_2/500°C; (c) Pd–Ti/SiO_2/500°C; (d) Pd–Nb/SiO_2/500°C; (e) Pd–Ce/SiO_2/500°C.

Table 2
The amounts of CO adsorption and the intensity ratios of multiply-bound band (A_m) to linearly-bound band (A_l) on various catalysts

Catalysts	Reduction temperature (°C)	CO/Pd	A_m/A_l
Pd/SiO$_2$	300	0.71	2.5
	500	0.48	5.5
Pd–Ti/SiO$_2$	300	0.55	3.8
	500	0.08	1.0
Pd–Nb/SiO$_2$	300	0.54	4.4
	500	0.08	1.2
Pd–Ce/SiO$_2$	300	0.50	3.9
	500	0.10	1.5

(1995–1975 cm^{-1}), isolated-bridged (1960–1925 cm^{-1}), and tri-coordinated (1890–1870 cm^{-1}) modes [17]. The latter three modes represent the multiply-bound CO.

On Pd/SiO$_2$, the amount of CO adsorption decreases and the area ratio, A_m/A_l, increases from 2.5 to 5.5 when the reduction temperature is raised from 300 to 500°C. This is apparently due to the sintering of Pd particles. In the case of Pd–X/SiO$_2$, the CO uptake is seen to markedly decrease after reduction at 500°C, which is a typical phenomenon observed with the SMSI catalysts [18], therefore suggesting that the Pd surface is additionally modified by the oxides.

The addition of metal oxides to Pd/SiO$_2$ also changes the characteristic CO adsorption modes on the Pd surface. That is, the area ratio, A_m/A_l, on Pd–X/SiO$_2$ decreases after reduction at 500°C, which is an opposite trend to the case of Pd/SiO$_2$. The A_m/A_l ratio decreases in the order of Pd–Ce/SiO$_2$ > Pd–Nb/SiO$_2$ > Pd–Ti/SiO$_2$. It is notable in Fig. 3 that the decrease in the A_m/A_l ratio is mostly due to the disappearance of the band below 1900 cm^{-1} assigned to the tri-coordinated mode. In the case of Pd–Ti/SiO$_2$, the band at 1995–1975 cm^{-1} due to the compressed-bridged CO mode is also reduced.

We believe that the metal oxides play two roles on the Pd surface: the retardation of the Pd sintering and the blocking of CO adsorption in the multiply-bound mode. The latter role is possible when the oxides migrate onto the Pd surface after the high temperature reduction, which in fact is observed with the oxide-supported catalysts showing the SMSI phenomenon [19].

Table 3
The intensity ratios of XPS peaks for X (=Ti$_{3d}$, Nb$_{3d}$, and Ce$_{3d}$) and Pd$_{3d}$ on various catalysts

	Reduction temperature (°C)	Ratio
Ti$_{3d}$/Pd$_{3d}$	300	1.15
	500	2.38
Nb$_{3d}$/Pd$_{3d}$	300	1.18
	500	2.13
Ce$_{3d}$/Pd$_{3d}$	300	1.30
	500	2.08

3.3. XPS and TPD

To estimate the amounts of metal oxides possibly located on the Pd surface, we have measured the XPS of Pd–X/SiO$_2$ and compared the intensity ratios of peaks corresponding to X (=Ti$_{3d}$, Nb$_{3d}$, and Ce$_{3d}$) and Pd$_{3d}$ for different reduction temperatures. Table 3 indicates that the X/Pd ratios are consistently higher when the catalysts are reduced at 500°C instead of 300°C, thus supporting that metal oxides are highly populated on the Pd surface after reduction at 500°C. Taking the peak ratio as an indicator for the oxide population, we may conclude that the oxide covers the Pd surface in the order of Pd–Ce/SiO$_2$ < Pd–Nb/SiO$_2$ < Pd–Ti/SiO$_2$.

We have also compared the locations of the Pd$_{3d}$ peak on the catalysts reduced at 500°C. In Fig. 4, the peak at 334.9 eV observed on Pd/SiO$_2$ is shifted to lower energies by about 0.3 eV on Pd–X/SiO$_2$. The

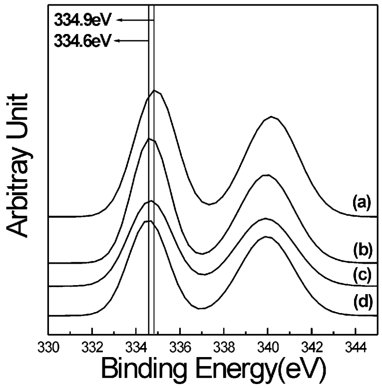

Fig. 4. XPS of Pd$_{3d}$ on various catalysts: (a) Pd/SiO$_2$/500°C; (b) Pd–Ti/SiO$_2$/500°C; (c) Pd–Nb/SiO$_2$/500°C; (d) Pd–Ce/SiO$_2$/500°C.

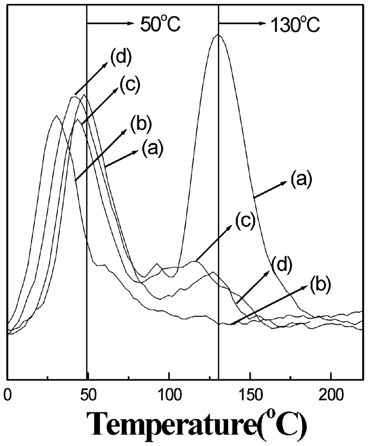

Fig. 5. Ethylene-TPD from various catalysts: (a) Pd/SiO_2/300°C; (b) $Pd–Ti/SiO_2$/500°C; (c) $Pd–Nb/SiO_2$/500°C; (d) $Pd–Ce/SiO_2$/500°C.

result contrasts to the one observed with the Si-modified Pd catalyst reported previously [6], where the peak was shifted to higher energies by 0.2 eV with Si addition. In that work, it was concluded that the Pd–Si alloy was not formed because the alloy formation usually showed the shift by more than 1 eV.

In this work, however, the shift by 0.3 eV should be regarded significant because the similar peak shift, both in respect to direction and extent, was observed with the catalysts showing the SMSI phenomenon, e.g., Pt/TiO_2 and Rh/TiO_2 [20]. The peak is shifted because metal oxides, which become rich with electron after the partial reduction at 500°C, donate electrons to the Pd surface.

In Fig. 5, Pd/SiO_2 reduced at 300°C shows two peaks of ethylene TPD from the Pd surface: one (Peak I) at 45°C originating from the di-σ C_2H_4 species, ethylidene, and the other (Peak II) at 130°C due to the triply-bound species, ethylidyne [21]. The TPD peaks change in two ways on $Pd–X/SiO_2$: the suppression of Peak II and the shift of Peak I to lower temperatures.

The suppression of Peak II 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 as suggested by the above IR and XPS results. The shift of Peak I to lower temperatures indicates that the ethylene adsorption is weakened by the oxide addition, which occurs when electrons are donated from the oxide to the Pd surface. Again, this trend agrees with the XPS result. Among the oxide-modified catalysts, $Pd–Ti/SiO_2$ shows the above changes most significantly as Peak II had almost disappeared and Peak I shifted to the largest extent.

3.4. *The role of metal oxides*

Based on the above experimental evidences, we may conclude the following points about the behavior of metal oxides in the catalysts especially when they are reduced at 500°C. The metal oxides, partially reduced at 500°C, migrate onto the Pd surface to modify the surface in two ways: the geometrical decoration and the electronic modification of the surface. By the geometric decoration, the multiply-coordinated, large ensembles of the Pd surface are blocked by the oxides and consequently the ethylene adsorption in the multiply-bound mode is suppressed. The electronic modification of the Pd surface reduces the adsorption strength of ethylene on the Pd surface, which allows for the rapid desorption of the surface ethylene species produced by acetylene hydrogenation.

In acetylene hydrogenation, the reaction proceeds via three major routes according to the previous mechanistic studies [22–25]. Path I is the hydrogenation of acetylene to ethylene followed by desorption from the surface or further hydrogenation. Path II is the hydrogenation of acetylene to intermediates, such as ethylidyne, which do not yield ethylene but are directly hydrogenated to ethane. Path III is the polymerization of ethylene to produce polymer that eventually covers the surface leading to the catalyst deactivation.

Considering the reaction paths of acetylene hydrogenation, we may explain the role of the metal oxides in improving the performance of the Pd catalyst in the reaction. Metal oxides spread on the Pd surface after reduction at 500°C to retard the sintering of the dispersed Pd particles and block the multiply-coordinated sites of Pd. The latter effect suppresses Paths II and III so that the production of ethane and polymer is reduced and the ethylene selectivity is improved. The electronic interaction between metal oxides and Pd facilitates the desorption of ethylene produced on the Pd surface by Path I so that the ethylene selectivity is improved further.

4. Conclusion

We have examined transition-metal oxides as promoters of the Pd catalyst for acetylene hydrogenation and confirmed that they have positive effects on the catalyst performance after reduction at 500°C. This is due to the decoration of the Pd surface with metal oxides, which has the same SMSI effect as observed with the oxide-supported catalysts. From the experimental evidences, we may conclude the following about the promotional effect of the oxides:

1. The sintering of the dispersed Pd particles is retarded and consequently the catalyst activity is preserved even after the reduction at 500°C.
2. The ethylene selectivity of the Pd catalysts is improved significantly by the oxide addition particularly after the catalysts are reduced at 500°C.
3. The geometric blocking of the multiply-coordinated Pd sites by the metal oxide and the electronic interaction between the Pd surface and the oxide are responsible for the promotional effect of the oxides.
4. Among the three metal oxides examined in this study, Ti oxide showed the most promotional effect.

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