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# Microcalorimetric studies of $O_2$ and $C_2H_4$ adsorption on $Pd/SiO_2$ catalysts modified by Cu and Ag

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## Abstract

The microcalorimetric adsorption of $H_2$ and $O_2$ has been employed to probe the dispersion of metals and surface composition of the bimetallic Pd-Cu/$SiO_2$ and Pd-Ag/$SiO_2$ catalysts. In addition, the microcalorimetric adsorption of ethylene was carried out to study the effects of Cu and Ag on the adsorption of ethylene on reduced and oxidized Pd surfaces. It was found that the addition of Cu or Ag diluted the surface Pd sites. The heats of $O_2$ adsorption for Pd-Cu and Pd-Ag were approximately the averages between those for Pd and the second metal Cu and Ag, respectively, when the ratios of Cu/Pd and Ag/Pd are low (1:1). Moreover, the O/H ratio was found to be about 0.5 for the Pd-Cu/$SiO_2$ (1:1) and Pd-Ag/$SiO_2$ (1:1) samples, which was about the same for the Pd/$SiO_2$ sample. These results suggest the enrichment of Pd on the surfaces in the bimetallic Pd-Cu/$SiO_2$ (1:1) and Pd-Ag/$SiO_2$ (1:1) samples. On the other hand, the initial heats of $O_2$ adsorption for the Pd-Cu/$SiO_2$ (1:4) and Pd-Ag/$SiO_2$ (1:4) are approximately equal to those of the second metal Cu and Ag, respectively, revealing the enrichment of the second metals in these samples. The addition of Cu or Ag inhibited the formation of ethylidyne on the reduced Pd surface, and Ag was found to be more effective than Cu for this effect. The adsorption of ethylene on the oxidized Pd resulted in the serious oxidation of ethylene. The addition of Cu or Ag greatly reduced the oxidation of ethylene on the oxidized Pd. In this case, Cu was more effective than Ag in reducing the activity of oxygen for the oxidation of ethylene on the Pd surface. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Alloys are important catalysts for the conversion of hydrocarbons [1,2]. The formation of alloys or bimetallic clusters may dramatically change the activity and selectivity of many reactions for the conversion of hydrocarbons. For example, Pd-Ag catalysts exhibited high selectivity for the hydrodechlorination of 1,2-dichloroethane into ethylene [3] and Pd-Cu catalysts were active for the selective oxidation of propylene to acetone and ethylene to acetaldehyde [4]. In addition, Ag itself can be used to catalyze the oxidation of ethylene to ethylene oxide. These reactions involve the adsorption of ethylene on catalysts. Therefore, studies of surface species and energies for the adsorption of ethylene on the bimetallic catalysts are important as a fundamental database. In particular, these data may be essential in constructing general reaction mechanisms for the reactions involving the adsorption of olefins. Recently, Hill et al. studied the adsorption of ethylene on Pd-Sn/$SiO_2$ catalysts by combining microcalorimetric adsorption and infrared spectroscopy performed at temperatures from 173 to 300 K [5]. FT-IR results indicate that ethylidyne,

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π-bonded and di-σ-bonded ethylene species could be formed on the Pd/$SiO_2$ catalyst at room temperature [5,6].

In the present paper, we report the results of microcalorimetric adsorption of ethylene and oxygen on the Pd-Cu/$SiO_2$ and Pd-Ag/$SiO_2$ catalysts. The effects of oxygen on the surface species for the adsorption of ethylene were discussed.

## 2. Experimental

### 2.1. Catalyst preparation and treatment

The catalysts were prepared by the incipient wetness method. The support used was a Cab-o-sil fumed silica (EH-5) provided by Cabot Co. (IL, USA). The precursors used for preparing the Pd/$SiO_2$, Cu/$SiO_2$, Ag/$SiO_2$, Pd-Cu/$SiO_2$ and Pd-Ag/$SiO_2$ catalysts are tetraammine-palladium(II) nitrate (Aldrich, 42,382-3), copper nitrate (AR) and silver nitrate (AR). The loading of palladium in all the Pd/$SiO_2$, Pd-Cu/$SiO_2$ and Pd-Ag/$SiO_2$ catalysts was kept at 2 wt.%, while the atomic ratios of Pd to the second metal (Cu or Ag) were 1:1 and 1:4, respectively. The Cu/$SiO_2$ and Ag/$SiO_2$ catalysts had the loading of 8 wt.%. In a preparation, an aqueous solution containing the required amount of precursors was mixed with the silica support to form a gel. The gel was dried at room temperature for 24 h and then further dried at 393 K overnight. The dried samples were calcined in flowing $O_2$ at 573 K for 3 h.

### 2.2. Microcalorimetric adsorption

The measurements were performed at 313 K using a Tian–Calvet type heat-flux microcalorimeter. The calorimeter was connected to a volumetric system equipped with a Baratron capacitance manometer (precision: 0.001 Torr) for the pressure measurement and gas handling. The maximum apparent leak rate of the volumetric system (including calorimetric cells) was about $10^{-4}$ Torr/min in approximate 35 $cm^3$ (i.e. about $2 \times 10^{-4}$ μmol/min). The ultimate dynamic vacuum of the system was ca. $10^{-5}$ Torr.

The procedures for microcalorimetric adsorption have been described in detail elsewhere [7]. Briefly, the sample was reduced in situ in a microcalorimetric cell under highly pure $H_2$ in the static mode at 473 and 573 K for 1 h and 673 K for 3 h, during which the sample was flushed with fresh $H_2$ every hour. Then, the sample was outgassed at 673 K for 1 h. After the cell was cooled to room temperature, about 600 Torr highly pure helium was admitted into the system to minimize the possible surface contamination by leakage during thermal equilibrium (ca. 10 h). After thermal equilibrium was reached, the helium in the cell was evacuated. The microcalorimetric data were then collected by sequentially introducing small doses (1–10 μmol) of probe molecules ($H_2$, $O_2$, or $C_2H_4$) onto the sample until it became saturated (equilibrium pressure reached 5–6 Torr). The heat response for each dose was recorded as a function of time and integrated to determine the energy released (mJ). The amount of gas adsorbed (μmol) was determined volumetrically. The differential heat (kJ/mol), defined as the negative enthalpy change, was then calculated for each dose by dividing the heat released by the amount of gas adsorbed.

## 3. Results and discussion

### 3.1. Adsorption of hydrogen for the measurement of surface sites

Fig. 1 shows the results for the microcalorimetric adsorption of $H_2$ on the Pd/$SiO_2$, Cu/$SiO_2$ and Pd-Cu/$SiO_2$ catalysts. The initial heat and saturation coverage for the 2% Pd/$SiO_2$ catalyst are 96 kJ/mol and 65 μmol/g, respectively. $H_2$ adsorbs weakly on the Cu/$SiO_2$ catalyst with the very low coverage of only 3.5 μmol/g. The plot of differential heat versus $H_2$

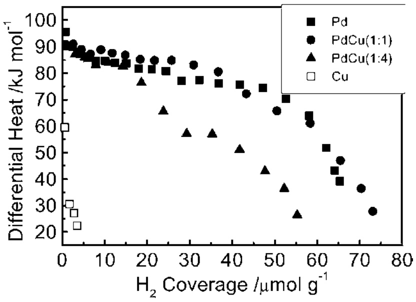


Fig. 1. Differential heat vs. adsorbate coverage for two adsorption at room temperature on the catalysts 2% Pd/$SiO_2$ (■); Pd-Cu (1:1)/$SiO_2$ (●); Pd-Cu (1:4)/$SiO_2$ (▲); 8% Cu/$SiO_2$ (□).

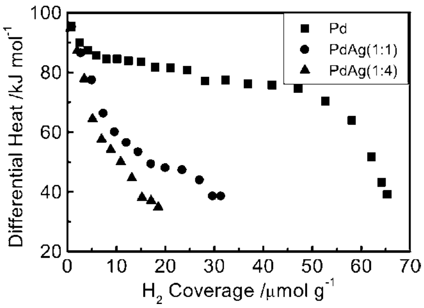
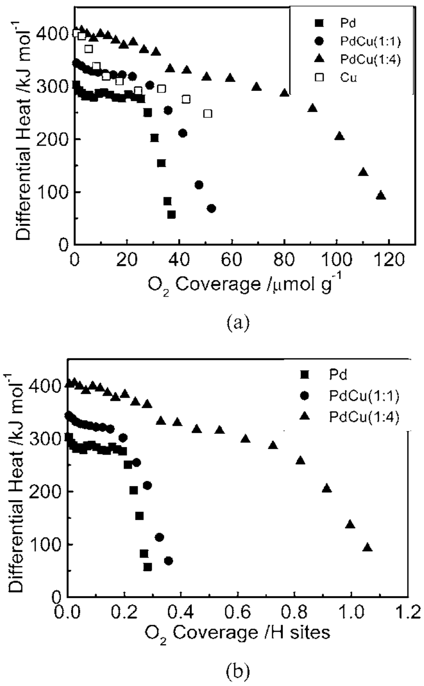


Fig. 2. Differential heat vs. adsorbate coverage for $H_2$ adsorption at room temperature on the catalysts 2% Pd/$SiO_2$ (■); Pd-Ag (1:1)/$SiO_2$ (●); Pd-Ag (1:4)/$SiO_2$ (▲).

coverage for the Pd-Cu (1:1)/$SiO_2$ is similar to that for the Pd/$SiO_2$, indicating that the surface Pd sites were almost not affected by the presence of Cu in the Pd-Cu (1:1)/$SiO_2$ sample for the adsorption of $H_2$. However, when the Cu/Pd ratio was increased to 4, the number of surface Pd sites and the strength of most Pd sites for $H_2$ adsorption were significantly decreased.

The differential heats versus adsorbate coverage for the adsorption of $H_2$ on the Pd/$SiO_2$ and Pd-Ag/$SiO_2$ catalysts are compared in Fig. 2. Ag/$SiO_2$ does not adsorb $H_2$. It is seen from Fig. 2 that the number of Pd sites and the strength of Pd sites for $H_2$ adsorption were substantially decreased in the Pd-Ag/$SiO_2$ samples as compared to the Pd/$SiO_2$. Moreover, the number of surface Pd sites was further decreased with the increase of Ag in the Pd-Ag/$SiO_2$ samples. By comparing the results for $H_2$ adsorption on Pd-Cu/$SiO_2$ and Pd-Ag/$SiO_2$ catalysts, it is apparent that Ag has the stronger effect than Cu in modifying the properties of surface Pd atoms.

### *3.2. Adsorption of oxygen*

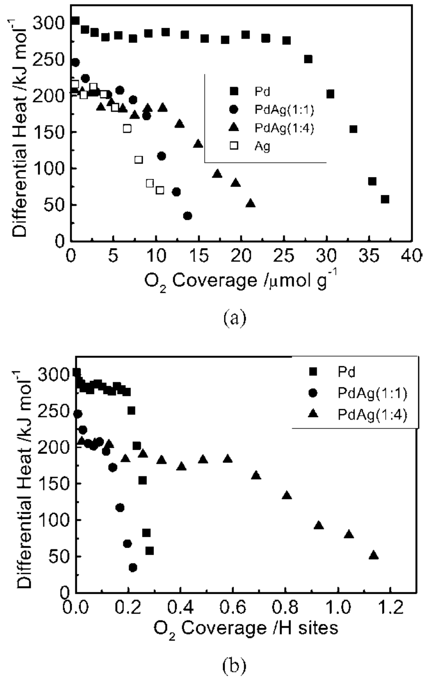


(a)

(b)

Fig. 3. Differential heat vs. adsorbate coverage for $O_2$ adsorption at room temperature on the catalysts 2% Pd/$SiO_2$ (■); Pd-Cu (1:1)/$SiO_2$ (●); Pd-Cu (1:4)/$SiO_2$ (▲); 8% Cu/$SiO_2$ (□). Units: (a) μmol adsorbed absorbate per gram of catalyst and (b) coverage as normalized to the saturation coverage of H.

Fig. 3a shows the results of microcalorimetric adsorption of $O_2$ on the Pd/$SiO_2$, Pd-Cu/$SiO_2$ and Cu/$SiO_2$ catalysts at room temperature. The adsorption of $O_2$ on the Pd/$SiO_2$ produces the initial heat of about 300 kJ/mol. The heat remains almost constant up to the coverage of 25 μmol/g. Then, the heat decreases sharply with the further increase of $O_2$ doses up to the saturation coverage of 37 μmol/g. The initial heat for $O_2$ adsorption on the Cu/$SiO_2$ sample is about 400 kJ/mol. It is interesting to note that the heat for $O_2$ adsorption on the Pd-Cu (1:1)/$SiO_2$ is about 345 kJ/mol, which can be taken as the average of the heats for $O_2$ adsorption on Pd and Cu. However, the initial heat for $O_2$ adsorption on the Pd-Cu (1:4)/$SiO_2$ is the same as that on Cu/$SiO_2$. Moreover, the coverage of $O_2$ on the Pd-Cu (1:4)/$SiO_2$ is greatly increased, indicating the enhanced dispersion of Cu by the presence of Pd. In Fig. 3b are shown the heats versus $O_2$ coverage as normalized to the surface sites titrated by $H_2$ adsorption for these samples (divided by saturation coverage of H atoms). The O/H ratio is found to be about 0.5 for the Pd/$SiO_2$ sample, indicating that an oxygen atom seems to occupy two Pd atoms on the surface. It should be mentioned that the O/H ratio for the Pd-Cu (1:1)/$SiO_2$ catalyst is also close to 0.5 (as if $O_2$ were only adsorbed on Pd), implying the enrichment of Pd on the surface in this sample. However, the average heat for the adsorption of $O_2$ on the Pd-Cu (1:1)/$SiO_2$ reveals the influence of Cu. The O/H ratio is greater than 2 for the Pd-Cu (1:4)/$SiO_2$ sample, demonstrating the substantial enrichment of Cu on the surface of the sample.



(a)

(b)

Fig. 4. Differential heat vs. adsorbate coverage for $O_2$ adsorption at room temperature on the catalysts 2% Pd/$SiO_2$ (■); Pd-Ag (1:1)/$SiO_2$ (●); Pd-Ag (1:4)/$SiO_2$ (▲); 8% Ag/$SiO_2$ (□). Units: (a) μmol adsorbed adsorbate per gram of catalyst and (b) coverage as normalized to the saturation coverage of H.

Fig. 4a shows the results of microcalorimetric adsorption of $O_2$ on the Pd-Ag/$SiO_2$ and Ag/$SiO_2$ catalysts at room temperature in comparison with that on Pd/$SiO_2$. $O_2$ adsorption on Ag/$SiO_2$ produces the initial heat of about 215 kJ/mol. $O_2$ adsorption on the Pd-Ag (1:1)/$SiO_2$ sample produces the initial heat of about 245 kJ/mol, which is about the average of the heats for $O_2$ adsorption on Ag and Pd. The initial heat for $O_2$ adsorption on the Pd-Ag (1:4)/$SiO_2$ is almost the same as that for $O_2$ adsorption on the Ag/$SiO_2$, but the $O_2$ coverage is significantly increased, indicating the enhanced dispersion of Ag by the presence of Pd. Differential heat versus $O_2$ coverage as normalized to the saturation coverage of H for the Pd-Ag/$SiO_2$ samples is shown in Fig. 4b. The O/H ratio is also approximately equal to 0.5 for the Pd-Ag (1:1)/$SiO_2$ catalyst, implying that the surface of the Pd-Ag alloy may be mainly covered by Pd. Similar to the case for the Pd-Cu (1:4)/$SiO_2$ sample, the O/H ratio of greater than 2 for the Pd-Ag (1:4)/$SiO_2$ sample indicates that the surface of the Pd-Ag alloy is mainly covered by Ag in the sample.

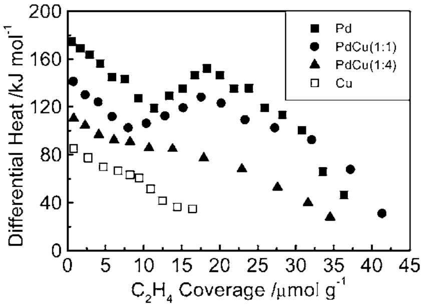


Fig. 5. Differential heat vs. adsorbate coverage for ethylene adsorption at room temperature on the catalysts 2% Pd/$SiO_2$ (■); Pd-Cu (1:1)/$SiO_2$ (●); Pd-Cu (1:4)/$SiO_2$ (▲); 8% Cu/$SiO_2$ (□).

### 3.3. Adsorption of ethylene

The results of microcalorimetric adsorption of ethylene on the Pd/$SiO_2$, Cu/$SiO_2$ and Pd-Cu/$SiO_2$ catalysts at room temperature are shown in Fig. 5. The initial heat of ethylene adsorption on the Pd/$SiO_2$ is 175 kJ/mol, which is attributed to the formation of surface ethylidyne and atomic hydrogen owing to the dissociation of adsorbed ethylene [5]. The apparent maximum of the adsorption heat around the ethylene coverage of 18 μmol/g is due to the evolution of gaseous ethane formed by the reaction of ethylene with surface hydrogen [8]. Adsorption of ethylene on the Cu/$SiO_2$ produces the initial heat of 85 kJ/mol, which can be ascribed to the formation of π-adsorbed species [9]. The shape of the heat of interaction versus coverage curve for ethylene adsorption for the Pd-Cu (1:1)/$SiO_2$ is similar to that for the Pd/$SiO_2$, indicating the formation of ethylidyne on the Pd-Cu (1:1)/$SiO_2$, too, but the lower heat for the Pd-Cu (1:1)/$SiO_2$ implies that some π- and/or di-σ-bonded ethylene species may also be formed on the Pd-Cu (1:1)/$SiO_2$. This result indicates that the dissociative adsorption of ethylene is partially inhibited by Cu in the Pd-Cu (1:1)/$SiO_2$ sample. When the Cu/Pd ratio increases to 4, the formation of ethylidyne is inhibited as evidenced by the disappearance of the maximum in the heat versus coverage curve for the adsorption of ethylene on the Pd-Cu (1:4)/$SiO_2$. The initial heat for the adsorption of ethylene on the Pd-Cu (1:4)/$SiO_2$

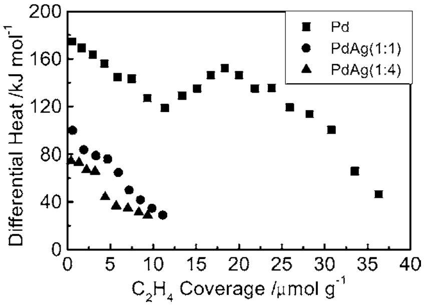


Fig. 6. Differential heat vs. adsorbate coverage for ethylene adsorption at room temperature on the catalysts 2% Pd/$SiO_2$ (■); Pd-Ag (1:1)/$SiO_2$ (●); Pd-Ag (1:4)/$SiO_2$ (▲).

is measured to be about 110 kJ/mol, which may be ascribed to the formation of surface di-σ- and π-bonded ethylene species.

The comparison of Pd-Ag/$SiO_2$ catalysts with Pd/$SiO_2$ for the adsorption of ethylene is depicted in Fig. 6. The adsorption of ethylene on Ag/$SiO_2$ is negligible. The initial heats for ethylene adsorption on the Pd-Ag (1:1)/$SiO_2$ and Pd-Ag (1:4)/$SiO_2$ are 100 and 74 kJ/mol, respectively, which are substantially lower than that on the Pd-Cu (1:4)/$SiO_2$ sample and may be attributed to the formation of π- and di-σ-bonded ethylene species. In particular, the initial heat of 74 kJ/mol for the ethylene adsorption on the Pd-Ag (1:4)/$SiO_2$ may be due to the formation of only π-species.

### 3.4. The effects of pre-adsorbed oxygen on the adsorption of ethylene

The heats versus adsorbate coverage for the adsorption of ethylene on the oxygen pre-covered Pd/$SiO_2$, Cu/$SiO_2$ and Pd-Cu/$SiO_2$ catalysts are shown in Fig. 7. The initial heat as high as 400 kJ/mol for the adsorption of ethylene on the O/Pd/$SiO_2$ indicates the serious oxidation of ethylene on the oxidized Pd at room temperature. The initial heat for the adsorption of ethylene on the O/Cu/$SiO_2$ is low (81 kJ/mol), implying the molecularly adsorbed ethylene on the oxidized Cu surface. The initial heat for the adsorption of ethylene on the O/Pd-Cu (1:1)/$SiO_2$ and O/Pd-Cu (1:4)/$SiO_2$ are 142 and 112 kJ/mol, respectively, which are much lower than the heat for ethylene adsorption on the oxidized Pd/$SiO_2$, indicating the fact that the activity of adsorbed oxygen on Pd is significantly inhibited by the presence of Cu.

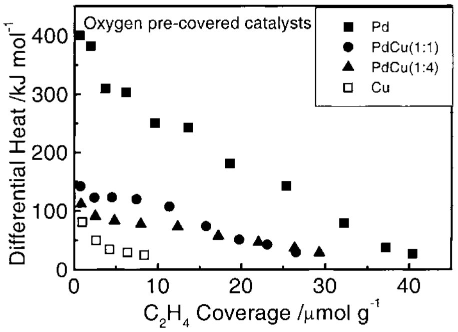


Fig. 7. Differential heat vs. adsorbate coverage for ethylene adsorption at room temperature on the oxygen pre-covered catalysts 2% Pd/$SiO_2$ (■); Pd-Cu (1:1)/$SiO_2$ (●); Pd-Cu (1:4)/$SiO_2$ (▲); 8% Cu/$SiO_2$ (□).

Fig. 8 shows the results for the adsorption of ethylene on the oxygen pre-covered Pd-Ag/$SiO_2$ and Ag/$SiO_2$ catalysts. The result for the ethylene adsorption on the O/Pd/$SiO_2$ is also shown for comparison. Although metallic Ag does not adsorb ethylene, the oxygen pre-covered Ag/$SiO_2$ sample does adsorb ethylene and produces the initial heat as high as 345 kJ/mol. This result implies that the surface oxygen species on Ag is much more active than that on Cu and ethylene may be oxidized on the O/Ag/$SiO_2$ at room temperature. However, the initial heats for the adsorption of ethylene on the O/Pd-Ag (1:1)/$SiO_2$ and O/Pd-Ag (1:4)/$SiO_2$ are 241 and 265 kJ/mol, respectively, which are much lower than those on the O/Pd/$SiO_2$

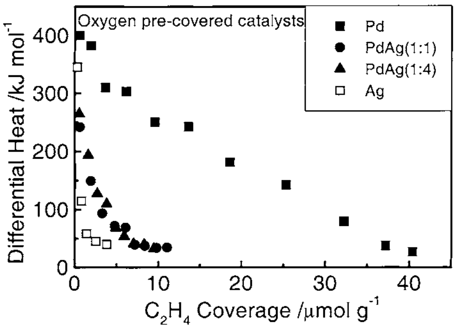


Fig. 8. Differential heat vs. adsorbate coverage for ethylene adsorption at room temperature on the oxygen pre-covered catalysts 2% Pd/$SiO_2$ (■); Pd-Ag (1:1)/$SiO_2$ (●); Pd-Ag (1:4)/$SiO_2$ (▲); 8% Ag/$SiO_2$ (□).

and O/Ag/$SiO_2$. These results demonstrate that the addition of Ag also reduces the activity of adsorbed oxygen on Pd, although not as effectively as Cu.

## 4. Conclusions

The addition of Cu or Ag dilutes the surface Pd sites. The bimetallic surfaces of Pd-Cu and Pd-Ag are enriched with Pd when the ratios of Cu/Pd and Ag/Pd are low (1:1), while they are enriched with Cu and Ag, respectively, when the ratios are high (1:4), as evidenced by the heat of $O_2$ adsorption and the H/O uptake ratios. The addition of Cu and Ag inhibits the formation of ethylidyne on Pd for the adsorption of ethylene at room temperature. This effect is more pronounced for Ag than for Cu. Pre-adsorption of oxygen on Cu has little influence on the formation of $\pi$-bonded species. Pre-adsorption of oxygen on Pd leads to the serious oxidation of ethylene. Although Ag/$SiO_2$ itself does not adsorb ethylene, the oxygen pre-covered Ag/$SiO_2$ produces the high initial heat for the adsorption of ethylene. The addition of Cu or Ag inhibits the oxidation of ethylene on the oxidized Pd surface, i.e. the activity of adsorbed oxygen on Pd can be substantially reduced by the presence of Cu or Ag. In this case, the effect of Cu on the inhibition of the oxidation of ethylene on the oxidized Pd is more pronounced than that of Ag.

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