Catalytic Activity of Highly Dispersed Palladium. III. The Effect of Added Zirconium Oxide upon Palladium Metal Surface Revealed by a Combined Infrared Spectroscopic and Thermal Desorption Study of Carbon Monoxide Adsorption

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A combined infrared spectroscopic (IR) and thermal desorption (TD) study of CO adsorption was carried out to reveal the nature of Pd surface which is modified by the addition of ZrO_2. The TD spectra of CO from SiO_2- or α-Al_2O_3-supported Pd showed two broad peaks, α at 340 K and β at 530 K. The addition of ZrO_2 in a range of atomic ratios of Zr/Pd=0.5—3.0 produced a new broad peak δ at 390—420 K and the β peak shifted toward higher temperature by 16—19 K. The IR spectra of CO on Pd/SiO_2 catalysts, consisting of two broad bands: A (2030—2070 cm^{-1}) and B (1880—1920 cm^{-1}), were modified by the addition of ZrO_2 to give rise to a new sharp band, B_h (1970—1985 cm^{-1}) and to make the A band narrower. From the correspondence of the variation in intensities and position of the IR bands with those in the fraction of coverage of CO with temperature, the α peak was correlated to the A band, the δ peak to the B_h band, and the β peak to the B band. The changes in the TD peaks and the IR bands caused by added ZrO_2 were semiquantitatively compared and are discussed in terms of the electronic and geometric effects; a high electron density state of Pd surface atoms as well as the formation of adsorption sites with specific structure is proposed. A brief study was made for the role of the sites in the catalytic hydrogenation of ethylene and cyclohexene.

In this series of studies, which aims at clarifying the support effect in heterogeneous catalysis, the remarkable role of ZrO_2 in the catalytic behavior of dispersed palladium has been pointed out.[1,2] The Pd metal surfaces, in the presence of ZrO_2, exhibited an enhanced activity for the cyclohexene hydrogenation, causing a change in kinetic behavior. The XPS study showed that the Pd metal atoms were slightly negatively charged as a consequence of electron transfer from ZrO_2 to the metal and that this was mainly responsible for their prominent activities. It was also found that the ZrO_2 brought Pd metal to a highly dispersed state and increased the percentage exposed. These effects might be realted to the preferential fromation of the active sites with peculiar structures. Such ZrO_2-affected Pd metal surfaces may give rise to specific adsorptive properties as well, since the interaction with admolecules is much influenced by the changes in structure and electronic state. Therefore, a combined infrared spectroscopic (IR) and thermal desorption (TD) study of CO adsorption was undertaken to ascertain the adsorptive behavior and, further, to prove the advantage of using CO as a sensitive probe for investigating the details of characteristics of the surface.

In the present study, attention was paid to the following points. First, numerous IR measurements of adsorbed CO on metal surfaces have shown that the position of absorption band changed markedly according to the preparation methods of dispersed metals such as the procedures of metal loading, pretreatment, *etc.*[3] However, such disturbing influences can be avoided or, at least, minimized, when the samples to be measured are prepared with the same procedure. In the present study, thus, the silica- and α-alumina-supported Pd, ZrO_2-added Pd/SiO_2 and Pd/α-Al_2O_3, and the ZrO_2-supported Pd were prepared in the same way as exactly as possible. The produced catalysts were characterized by the X-ray diffraction and CO chemisorption methods.

Secondly, the IR band frequencies are also affected not only by the interaction between admolecule and surface, but also by the interactions such as dipole-dipole coupling and/or direct repulsion between admolecules[4] and, therefore, by the fraction of surface coverage. Thus, in order to reveal the contribution of the metal support interaction on adsorption, it is desirable to make the influence of the latter as low as possible; this situation will be attained in the case that the spectra obtained at similar low fractions of coverage are compared with each other for the similar adsorbed states. In this regard, the combination of IR spectroscopy with TD technique which is able to distinguish among the adsorbed states is indispensable. The catalytic activities of the prepared catalysts were briefly examined for the hydrogenation of ethylene and cyclohexene.

Experimental

The Pd/SiO_2 (2.1% in weight) and ZrO_2-added catalysts were prepared in a manner similar to those employed previously for the Pd/α-Al_2O_3 and ZrO_2-added catalysts.[1,2] The Aerosil silica 130, obtained from the Nihon Aerosil Co., was washed with 0.1 mol dm^{-3} nitric acid and then rinsed thoroughly with ion-exchanged water. The catalysts thus prepared were pretreated *in situ* in the TD or IR cell by oxidation, reduction and then evacuation at the same temperature of 723 K. This reduction temperature was higher than 523 K, *viz.*, a temperature employed in pretreatment of the catalysts for the previous kinetic studies,[1,2] since the TD experiments required Pd surfaces which are stable and resistive for heating up to 700 K. The supported catalysts were characterized by the X-ray diffraction and CO chemisorption methods.

The apparatus used for the TD and IR experiments were almost the same as those reported previously.[5] In the TD study, the catalysts were exposed to a CO atmosphere at room temperature, cooled down to 78 K, and then evacuated at the same temperature before a TD run. The temperature of the catalysts was raised at a rate of 13 K $min.^{-1}$ Under similar

Table 1. Characterization of the catalysts and ZrO_2 effects upon turn-over frequency of ethylene and cyclohexene hydrogenation

Support	Zr/Pd ratio	Amount of CO adsorbed (at 273 K)	$D_{CO}^{a)}$/%	$D_X^{b)}$/nm	Turn-over frequency(N_t)$^{c)}$	
		molecule g-Pd^{-1}			$C_2H_4+H_2$	$C_6H_{10}+H_2$
SiO_2	0	3.23×10^{20}	5.7	84	1.7	—$^{d)}$
	0.5	4.38	7.7	52	2.3	—
	1.0	5.21	9.2	20	3.3	—
	3.0	7.37	13.0	15	6.4	—
α-Al_2O_3	0	0.95×10^{20}	1.7(2.3)$^{e)}$	108	(1.4)	0.1(0.1)$^{e)}$
	0.5	1.07	1.9(3.0)	90	(6.1)	0.7(0.7)
	2.5	1.65	2.9(5.0)	55	(6.9)	0.8(0.7)
ZrO_2	—	3.5×10^{20}	6.2(10.1)	30	7.5	1.3(1.2)

The values in parentheses were for the catalysts pretreated at 523 K.

a) Percentage exposed (dispersion) evaluated by assuming one CO admolecule on each Pd atom. b) Particle size derived from X-ray line broadening. c) Partial pressure of each reactant: 40 Torr; reaction temperatures: 301 K for cyclohexene hydrogenation and 273 K for ethylene hydrogenation. d) Because of the take-up of cyclohexene by SiO_2 support, a direct comparison under the same conditions was difficult. e) See Ref. 2.

adsorption conditions, the ZrO_2 and SiO_2 supports themselves gave rise to a single peak of CO around 255 and 287 K, respectively, but no peak at all above 300 K. When the pressure of introduced CO was high, these peaks were superposed on a part of the CO peak desorbed from Pd metal. Such contribution of the interfering peak was compensated by extracting the peak-height which corresponds to that from the supports. In the IR study, CO was introduced at room temperature into the IR cell, and the spectra were recorded at the same temperature.

The catalytic hydrogenations of ethylene and cyclohexene were studied by using a closed circulation system up to 40 Torr (1 Torr=133.3 Pa) of partial pressure of each reactant and at temperatures between 273 and 301 K.

Results

Table 1 shows the observed characteristics of the supported Pd catalysts and ZrO_2-added catalysts. By the addition of ZrO_2, the particle size of Pd metals changed from 84 to 15 nm for Pd/SiO_2 and from 108 to 55 nm for Pd/α-Al_2O_3 catalysts. These changes were reflected in an increase in the percentage exposed. Table 1 also shows the turn-over frequency, N_t, of ethylene and cyclohexene hydrogenations; these values were evaluated on the assumption that the number of surface Pd atoms is equal to that of CO molecules adsorbed. With increasing Zr/Pd ratio, N_t's raised considerably for both reactions; at Zr/Pd=2.5—3, it increased by factors of 4—5 for the ethylene hydrogenation and 7—8 for the cyclohexene hydrogenation. As is shown by parentheses, the N_t's for the cyclohexene hydrogenation were the same within experimental error independent of pretreatment temperature: 523 or 723 K.

TD Spectra. Figure 1 shows the TD spectra of CO adsorbed on the Pd/SiO_2 catalysts. Two peaks were mainly observed, at 330—350 K (α peak) and at around 530 K (β peak); the latter peak had a shoulder γ around 600 K. Above 600 K, the spectra contained small peaks due to CO_2. The surface coverage, θ, was defined as the ratio of the amount of CO adsorbed to that at saturation. The β-peak was saturated at around θ=0.4, whereas the α-peak continued to increase with increasing θ. Figure 2 shows the TD spectra of CO desorbed from the ZrO_2-added Pd/SiO_2 catalysts. By the addition of ZrO_2 at a ratio of Zr/Pd=1, two main peaks were again observed but a peak appeared clearly at *ca.* 420 K (δ peak), and the β peak shifted toward high temperature by 16 K. With an increase in θ, the saturation of the β-peak occurred, followed by a considerable growth of the α, γ, and δ-peaks. Figure 3 shows the TD spectra at Zr/Pd=3. The δ-peak was more evidently observed, and the β-peak appeared at 547 K.

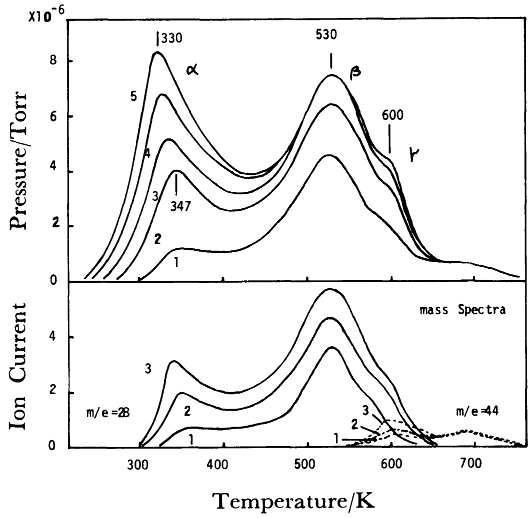


Fig. 1. Thermal desorption spectra of CO from Pd/SiO_2 catalyst.
1. θ=0.13, 2. 0.26, 3. 0.35, 4. 0.49, 5. 0.59.

In continuation of the previous studies,[1,2] the α-alumina was employed as support, and the effects of added ZrO_2 were examined. As is shown in Fig. 4, the Pd metals on α-Al_2O_3 provided almost identical TD spectra of CO with those obtained by using the silica support. When ZrO_2 was loaded at a ratio of Zr/Pd=0.5 on this surface, a broad hump emerged at around 400 K,

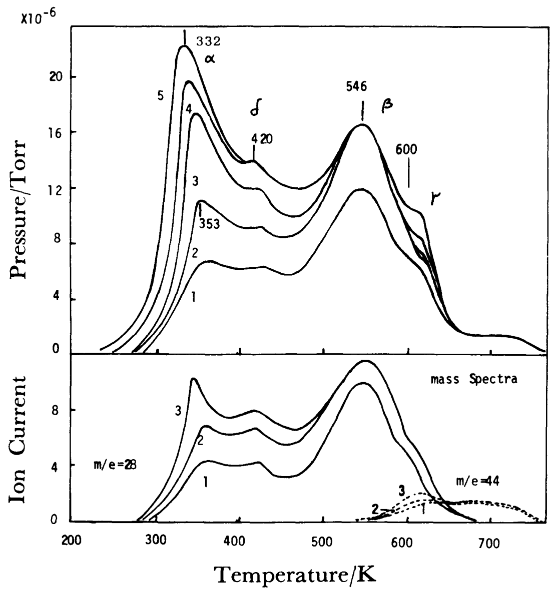


Fig. 2. TD spectra of CO from ZrO_2-added Pd/SiO_2 catalyst (Zr/Pd=1.0).
1. θ=0.15, 2. 0.20, 3. 0.34, 4. 0.47, 5. 0.58.

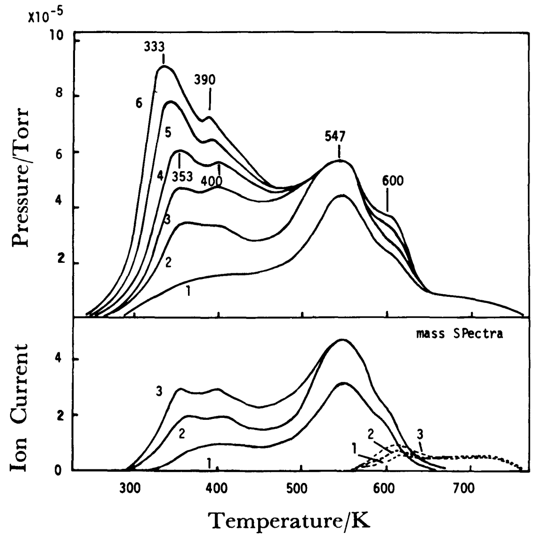


Fig. 3. TD spectra of CO from ZrO_2-added Pd/SiO_2 catalyst (Zr/Pd=3.0).
1. θ=0.07, 2. 0.21, 3. 0.31, 4. 0.47, 5. 0.54.

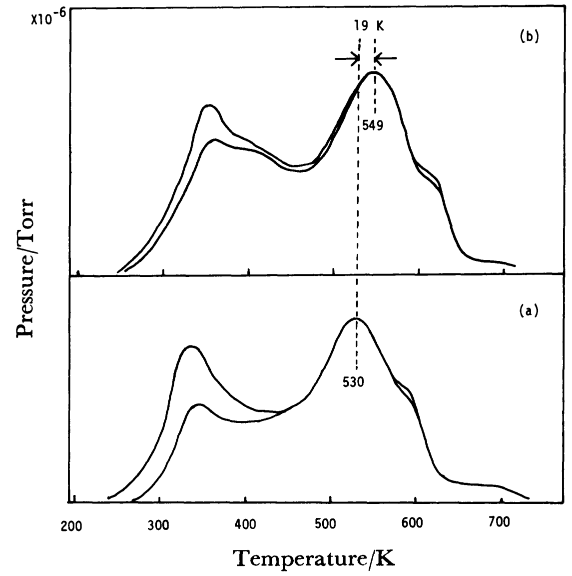


Fig. 4. Change in TD spectra of CO with ZrO_2 addition.
a) $Pd/\alpha-Al_2O_3$; 1. θ=0.50, 2. θ=0.69, b) ZrO_2-added Pd/α-Al_2O_3 (Zr/Pd=0.5); 1. θ=0.58,2. θ=0.61.

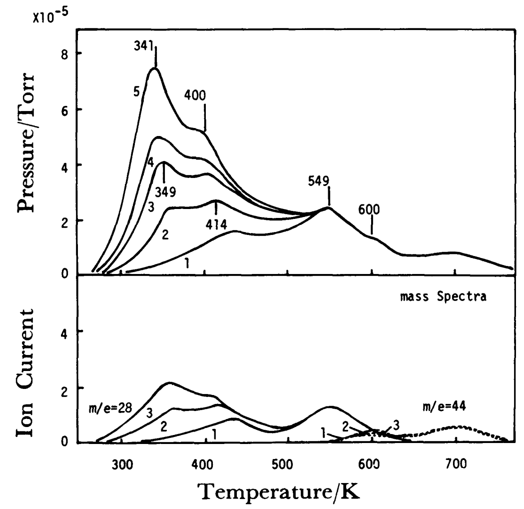


Fig. 5. TD spectra of CO from ZrO_2-supported Pd catalyst.
1. θ=0.08, 2. 0.12, 3. 0.26, 4. 0.40, 5. 0.59.

and the β-peak shifted by 19 K toward higher temperature. It is to be noted that the ZrO_2 effect was analogous on both inert supports.

The relative intensity of the δ-peak was enhanced with an increase in the Zr/Pd ratio. As the other extreme, ZrO_2 was used as support; as is shown in Fig. 5, the corresponding δ-peak was clearly observed, and the β-peak appeared at 549 K.

IR Spectra. Figure 6 shows the IR spectra of CO adsorbed at room temperature on the silica-supported Pd surface and their changes upon subsequent heat treatment. As is reported elsewhere,[3] two broad bands, A and B, appeared; with an increase in the amount of CO adsorbed, the A-band at higher frequency shifted from 2029 to 2071 cm^{-1}, and the B band at lower frequency from 1880 to 1920 cm^{-1}. When gaseous CO was evacuated at room temperature, the A-band was remarkably attenuated with a shift to 2045 cm^{-1}, whereas the B-band was weakened to a lesser extent, giving a band at 1903 cm^{-1}. Further evacuation at 453 K caused almost complete disappearance of the A-band, but the B-band remained stable up to 533 K. The variations of IR spectra upon evacuation at elevated temperature occurred in a reverse way as the increase of the CO exposure.

The IR spectra for the ZrO_2-added catalysts are shown in Fig. 7. At Zr/Pd=0.1, the spectra below 2000 cm^{-1} exhibited a sharp band, B_H, centered at 1970 cm^{-1} and a shoulder tailing toward lower frequency, whereas the A-band appeared at 2097 cm^{-1} with narrow peak width. These spectral features became more distinct with

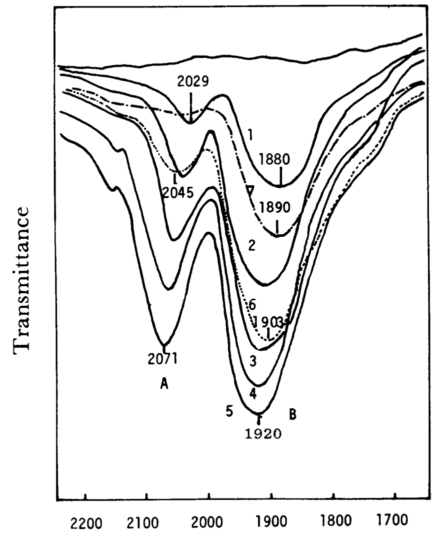


Fig. 6. IR spectra of CO adsorbed on Pd/SiO$_2$ catalyst and their changes upon evacuation at different temperatures.
1. θ=0.21, 2. 0.35, 3. 0.47, 4. 0.59, 5. 0.67, 6. evacuated at 298 K for 20 min, 7. at 453 K for 20 min.

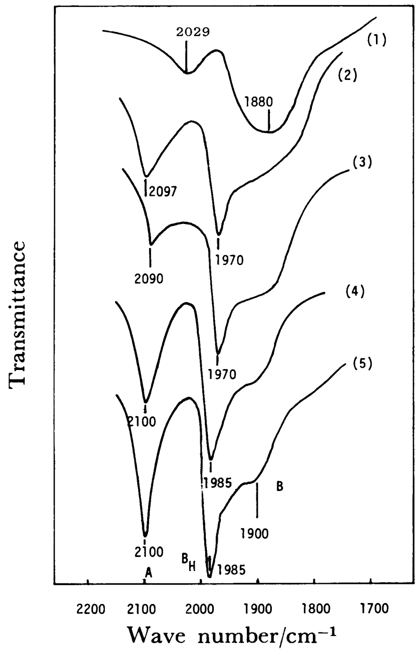


Fig. 7. Changes in IR spectra of adsorbed CO with increasing ratio of Zr/Pd ratio.
1. Zr/Pd=0 (Pd/SiO$_2$); θ=0.21, 2. 0.1; 0.2, 3. 0.5; 0.22, 4. 1.0; 0.42, 5. 3.0; 0.68.

increasing Zr/Pd ratio; the addition of ZrO$_2$ at Zr/Pd=0.5—3.0 produced the B$_H$-band at 1970—1985 cm^{-1} and the A-band at 2090—2100 cm^{-1}. At the different exposures of CO, the spectral changes caused by added ZrO$_2$ were clearly observed, which indicated that the above-mentioned features are not coverage-dependent but are due to the intrinsic effect of added ZrO$_2$ oxide.

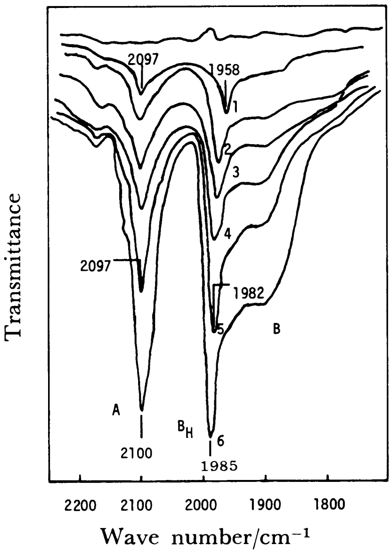


Fig. 8. IR spectra of CO on the ZrO$_2$-added catalyst (Zr/Pd=3.0) as a function of CO exposure.
1. θ=0.21. 2. 0.34, 3. 0.48, 4. 0.54, 5. 0.68, 6. 0.80.

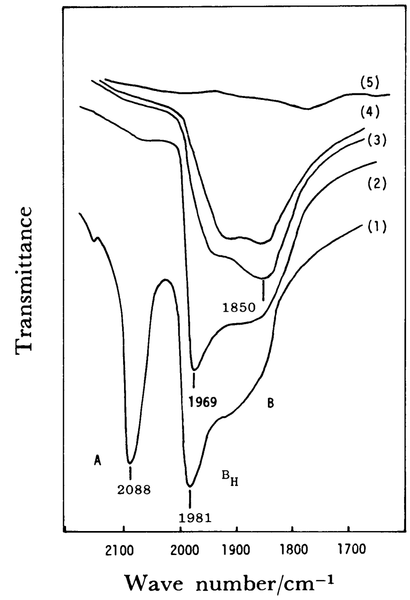


Fig. 9. Variations in IR spectra with evacuation temperature.
ZrO$_2$-added catalyst (Zr/Pd=0.5)
1. before evacuation (P_{CO}=1 Torr), 2. evacuated at 298 K for 40 min, 3. at 423 K for 20 min, 4, at 573 K for 30 min, 5. at 673 K for 20 min.

The IR spectra of the ZrO$_2$-added catalyst as a function of the CO exposure are shown in Fig. 8. The catalysts with the Zr/Pd ratio greater than 1.0 clearly exhibited ZrO$_2$-affected spectra even at low CO exposure, and, with increasing CO exposure, both A- and B$_H$-bands shifted to a lesser extent, in contrast to a large shift in the ZrO$_2$-absent catalysts. It is to be noted that the behavior of the band developments with CO exposure were different. Figure 9 shows the spectral variation upon heat treatment at different temperatures after CO adsorption at room temperature. For the catalyst with

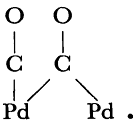
Zr/Pd=0.5, evacuation at 298 K caused the preferential and complete removal of the A-band, and further evacuation at 423 K resulted in the almost complete disappearance of the B_H band. Thanks to this evacuation, the remaining band, B, clearly manifested itself at an absorption frequency of 1850 cm^{-1}. Evacuation at 673 K annihilated completely the IR spectra in this region but produced a band around 1500 cm^{-1}, probably ascribable to the carbon dioxide species formed by disproportionation; such a result is in agreement with the TD results.

Discussion

In the absence of ZrO_2, the IR and TD spectra each provided two broad bands and peaks; these exhibited the corresponding changes upon increasing the amount of adsorbed CO as well as upon evacuation at different temperatures. The intensity of the A band in the IR spectra continued to increase above $\theta=0.4$ and was easily removed by evacuation at 300 K; this seems to have a common base with the TD α-peak which is present only at high surface coverage and in lower temperature. Since the B-band was produced first and resisted heating up to 550 K, it is evident that this band is associated with the TD β and γ-peaks appearing at low coverage and in higher temperature. The remarkable effects of the added ZrO_2 upon the CO adsorption on the Pd surfaces were well reflected by the generation of the sharp B_H band at 1980 cm^{-1} and the clearer appearance of the δ-peak desorbed at an intermediate temperature region.

In the Pd carbonyl complexes, a linearly-coordinated CO[6] was found to have a stretching frequency at 2050—2169 cm^{-1}, whereas the three-fold coordinated CO produced the frequency at 1800 cm^{-1} or below.[7] Furthermore, many studies of CO adsorbed on Pd metals have shown that the absorption band of CO in the 2050—2100 cm^{-1} range is the stretching vibration of a linearly-bonded CO, whereas the band of a range 2000—1800 cm^{-1} is associated with the multiply-bonded CO such as a bridged one.[8—18] This classification allows us to assign the B_H- and B-bands to the C–O stretching frequency of CO coordinated on multiple Pd atoms and the A-band to that coordinated linearly.

Kokes *et al.*[15] suggested that a stretching frequency of 1970 cm^{-1}, corresponding to the characteristic B_H band, is due to the bridge-bonded CO which shares one of two Pd atoms with a linearly bonded CO, *viz.*,



This assignment, however, does not seem to hold for in the present case, since the B_H-band still remained after the linear CO was completely removed by evacuation. Boudart *et al.*[16] obtained a band of 1980 cm^{-1} as a shoulder at CO pressure of as high as 300 Torr on the silica-supported Pd, suggesting that the band is ascribable to intermolecular interaction as a result of the compression of the admolecule and is favored for the larger Pd particles. However, the present results showed that the spectral features could be distinguished depending on the absence or presence of ZrO_2 component, irrespective of the CO coverage. Furthermore, Table 1 indicates the opposite trend as to the particle-size effect; the B_H-band became intensive with the decrease in size.

In a recent combined IR-reflection absorption and LEED study using single crystals of Pd which expose the (100), (111), or (210) surface, Bradshaw and Hoffmann[19] showed that the C–O stretching vibrational frequency in the region 1880—1970 cm^{-1} was observed for $\theta<0.5$ and CO is adsorbed on the two-fold coordination sites, which exist as bridge-site on the (100) plane as well as the (210) surface as the stepped (100) plane, whereas the frequency in the region 1800—1880 cm^{-1} was only observed for $\theta<0.3$ and CO is adsorbed on the three-fold coordination sites on the (111) surface. They also showed that, on the (100) surface, the band associated with a linear-bonded CO appeared at 2096 cm^{-1} even for $\theta\cong0.5$ in the case of the CO adlayer of poor ordering. The present IR spectra show that the IR band below 2000 cm^{-1} for Pd/SiO_2 catalyst covered broadly the range of the band for the ZrO_2-added catalysts, and the B-band still existed even in the presence of ZrO_2 (as a shoulder around 1880 cm^{-1}), thereby suggesting that the ZrO_2 effect can be related to the remarkable development of the narrow B_H-band. Thus, the consolidation of the above assignment and the fact that the B_H-band grew with increasing Zr/Pd ratio for similar CO coverage, as is shown in Fig. 7, lead to the consideration that the ZrO_2-affected Pd metal surfaces possess two-fold coordination sites of high density. This might be expected in case that the (100) plane and/or high index planes such as (210) were preferentially exposed, for instance, relative to the (111) plane. However, the extraordinarily narrow B_H band seems to reflect the existence of more specific dual sites such as isolated ones. The previous study showed that Pd metal atoms are able to interact strongly with ZrO_2 through the oxygen atoms.[2] When such incorporation of the metal with the oxide is taken into account, it is not unreasonable to consider that the ZrO_2 addition promoted the formation of the sites which have arrangements distinguishable from the usual largely-extended flat planes, *e.g.*, those like facets confined partially by ZrO_2 or a pair of protruded Pd atoms.

In the TD spectra, the position of the β-CO desorption peak remained almost unchanged as the CO coverage increased. This invariance is in agreement with the view that the CO desorption obeys the first-order kinetics.[20] Therefore, the shift of CO-desorption peak to higher temperature side by the presence of ZrO_2 component is indicative of the formation of stronger bonds between Pd metal and CO, since the adsorption of CO on Pd surfaces takes place *via* a nonactivated process.[21]

The β-CO corresponds to the CO remaining after evacuation at around 423 K, and the IR spectra gave rise to the absorption band at 1890 cm^{-1} for the Pd/SiO_2 catalysts and the band at 1850 cm^{-1} for the ZrO_2-added Pd/SiO_2 (Zr/Pd=0.5—3.0) catalysts. The presence of ZrO_2 actually caused a shift of the absorption band to lower frequency, at least by 40 cm^{-1}. The direction of respective variation in the TD and IR spectra is in line with the generally accepted view in which the weakening of bonds between C and O atoms resulted in the strenghtening of the admolecule-surface bonding, as is accounted for in terms of a back-donation of a metal electron into the $2\pi^*$ orbital of the molecule.

Since the β-state corresponds to that of CO at a small coverage, it is considered that the effects of intermolecular interaction upon the IR-band frequency and TD-peak position are safely minimized. Thus, the above-mentioned shift appears to reflect the changes in an intrinsic metal-admolecule interaction in the absence or presence of ZrO_2. Thus, the enhancement of back-donating electrons arises from a high electron density of Pd metal atoms, which is indicative of electron transfer from ZrO_2 to the metal. This finding gives support to the previous conclusion obtained by using X-ray photoelectron spectroscopy.[2]

The variation in the heat of adsorption, ΔE, usually accompanies the shift of the C–O stretching vibrational frequency of the admolecule, ΔW. The experimental data on the CO–Pd systems[19,22,23] show that the energetic ratio of $\Delta W/\Delta E$ is retained in the range 1.5×10^{-2}—15×10^{-2}. The calculation for the present ZrO_2-caused shifts of the β-peak and B band showed that this ratio was about 7×10^{-2}, which falls within the region described above. From the shifts of the δ-peak and the B_H band, relative to the β-peak and B band respectively, the ratio was roughly estimated to be 3×10^{-2}. Such agreement gives support to the assignments for the TD peaks and IR bands. As to the α-peak, we need some caution, since the α-state present at low temperature is somewhat a function of evacuation time prior to the TD run as well depending on the validity of the correction in elimiating a contribution of interfering peaks which originate from the supports.

With CO exposure, the broad A-band due to a linearly-bonded CO moved to higher frequency for the Pd/SiO_2 catalysts, in agreement with the well-established view,[3] whereas the sharp A band for the ZrO_2-added catalysts showed a little shift. This invariance and narrowing of the peak seem to be an indication of ZrO_2 effects, suggesting that the CO accepts a compensative back-donation from the ZrO_2-affected Pd metal atoms or that it is adsorbed on the confined sites which make the molecule free from the neighbouring ones.

Thus, the ZrO_2 component exerts not only electronic influence but also some geometric effects, in the sense that the surface sites with specific structures are preferentially produced on the ZrO_2-added Pd metal. The previous study found that with increasing addition of ZrO_2 to $Pd/\alpha\text{-}Al_2O_3$ catalysts the change in the kinetic parameters of the cyclohexene hydrogenation became negligibly small near a ratio of $Zr/Pd=0.5$, whereas the turn-over frequency continued to increase. It is likely that this can be correlated with the increase in the number of the specific sites. It is of interest to see that the ZrO_2 effects appear in the hydrogenation of unsaturated hydrocarbons such as ethylene, *cis*-2-butene and cyclohexene. The relative catalytic activities of the ZrO_2-added $Pd/\alpha\text{-}Al_2O_3$ catalysts with reference to $Pd/\alpha\text{-}Al_2O_3$ catalysts were increased with increasing dispersion (percentage exposed) in similar way for the hydrogenation of these olefines.[24]

Finally, in a recent IR study in connection with the catalytic hydrogenation of CO, Vannice *et al.*[25] showed that Pd metals on TiO_2 behave as in the case of the metal in Pt/TiO_2 catalysts; the strong metal-support interaction (SMSI) effect was generated after heating at 773 K such that the catalytic activity as well as the adsorptive properties was drastically reduced in spite of the presence of Pd metal particles with considerable surface area. In the present system, however, we observed little SMSI effect. The N_t for the cyclohexene hydrogenation was almost the same, independent of pretreatment temperature, *i.e.*, 1.2 for the 523 K-reduced Pd/ZrO_2 and 1.3 for the 723 K-treated one. Although a detailed comparison is needed, this fact seems to reflect a moderate interaction of the Zr cation through oxygen atoms with the metal, leading to a favorable catalytic effect, compared with an overly strong interaction of the Ti cation.

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