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Hydrogenation of Carbon Monoxide, Aldehydes, and Unsaturated Hydrocarbons on Titania-Supported Palladium Catalysts

Jihong Wu,* Masaki Funakoshi, Hidetoshi Nagamoto, Hiroshi Komiyama, and Hakuai Inoue
Department of Chemical Engineering, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo, 113

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Pd/TiO_2 catalysts prepared by different methods showed quite different catalytic activities in the hydrogenation of CO and other unsaturated compounds. The catalyst prepared by coprecipitation of Pd acetate and titanium tetraisopropoxide contained smaller Pd particles than those in catalysts prepared by impregnation methods. In the hydrogenation of CO, activities of the catalysts increased with increase in the Pd dispersion. The coprecipitated catalyst was much more active for this reaction than the other catalysts and showed high activity for methanol formation under normal pressure. In the hydrogenation of propionaldehyde to 1-propanol, the catalysts showed similar behavior to that in the CO/H_2 reaction. However, in hydrogenation of C=C double bonds, the activity order of the catalysts was reverse. Higher activity was obtained on the impregnated catalysts with larger Pd particle size and this trend was stronger in hydrogenation of the conjugated butadiene and C=C bond in acrylaldehyde than in the hydrogenation of ethylene.

Pd is widely used as a catalyst for the hydrogenation of various compounds. In some cases, supported Pd exhibits catalytic behavior much different from that of the bulk metal, and its activity and selectivity are quite sensitive to the nature of the supporting materials or other factors in preparation. Much research has been done concerning this problem. However, there is currently no agreement about a reliable way of describing the changes observed in the catalytic properties of a supported metal. In the case of Pd, hydrogenation of carbon monoxide is often studied for this purpose. Catalysts of Pd supported on various oxides were found to have very different activity and selectivity to this reaction.[1,2] Based on information obtained from the CO/H_2 reaction, there are mainly two ways of interpreting such variations in catalytic activity. One concerns the changes in the supported state of Pd caused by the interaction between Pd and the support, as suggested in the researches by Driessen[3] or by Fleisch.[4] On the other hand, some authors[5] have explained the support effect by the concept of ensemble effect wherein the support provides specific sites directly involved in the reaction rather than by considering changes in Pd. In the present work, we approach this problem from an alternate point of view. Titania-supported Pd catalysts with different Pd dispersions were prepared by coprecipitation and impregnation methods. The catalytic properties of these catalysts were investigated in hydrogenation of carbon monoxide, acrylaldehyde, propionaldehyde, 1,4-butadiene, and ethylene. The effect of Pd dispersion over titania was discussed on the basis of the activity order of the catalysts observed in the various reactions.

Experimental

Catalyst. The Pd/TiO_2 catalysts were prepared by three methods. (The resulting catalysts are denoted as A, B, and C respectively.) Catalyst A was prepared by coprecipitation by hydrolysis of $Ti(O\text{-}Pr^i)_4$ in its ether solution with $Pd(OAc)_2$. Diethyl ether was found to be a suitable solvent for the preparation, since alcoholic solvents such as methanol, ethanol, and propanols reduced the Pd salts and made it difficult to obtain a stable solution prior to the hydrolysis step. As soon as water was added to the solution hydrolysis took place. The yellow-brown color of $Pd(OAc)_2$ rapidly faded away from the solution along with the solid formation, indicating that the Pd salt had been adsorbed rapidly by the solid produced. Catalyst B was prepared by impregnating a commercial TiO_2 support (FA-50, 10 $m^2\,g^{-1}$, anatase, from Kogakogyo Corp.) with an ether solution of $Pd(OAc)_2$. Excess liquid was removed by evaporation. Catalyst C was prepared by impregnating the same FA-50 TiO_2 with a solution of $PdCl_2$ (0.25 ml/g-TiO_2), using the aqueous incipient wetness technique suggested by Tauster et al.[6] After coprecipitation or impregnation, the catalysts were dried in air at about 150 °C and then treated at assigned temperatures for use in the reactions.

Reaction Procedure. Reactions were carried out in conventional flow reactors and the products were analyzed by gas chromatography. For the hydrogenation of CO, a VZ-10 column was used to analyze hydrocarbons and a PEG-6000 column to analyze methanol and other oxygenates. For reactions of alkenes the products were also determined by a VZ-10 column, and for reactions of aldehydes a PEG-1000 column was used.

Other Measurements. Surface areas of catalysts were measured by N_2 adsorption. The irreversible adsorption of CO and H_2 was measured at room temperature using a pulse flow technique. Dispersion calculated from the adsorption amount of hydrogen (the atomic ratio H_{ad}/Pd) was used as the criterion to evaluate the specific activity of the catalysts. Measurements by X-ray diffraction and electron microscopy were also performed for characterization of the catalysts.

Results

Characterization of Catalysts. The different preparation methods resulted in catalysts with remarkably different Pd dispersions. Average Pd particle size calculated from the line broadening of the X-ray diffraction peak of Pd(111) are shown in Table 1. The measured surface area and the adsorption properties of the catalysts are also given in that table. Catalyst A, pre-

Table 1. Properties of Catalysts

Catalysts	Surf. area/ $m^2 g^{-1}$	Pd particle size from XRD/Å	Dispersion (H/Pd)
5.6% A H_2 300 °C 3 h	207	45	0.67
5.2% A[a] H_2 300 °C 3 h		51	0.54
1.7% A H_2 300 °C 3 h		83	0.50
5.6% A air 300 °C 2 h/H_2 300 °C 0.3 h		65	0.32
5.6% A air 300 °C 2 h/H_2 300 °C 1 h		65	0.34
5.2% B H_2 300 °C 2 h	8.9	186	0.17
5.2% B air 300 °C 1 h/H_2 300 °C 1 h			0.15
4.4% C H_2 300 °C 2 h	8.9	285	0.067
4.4% C air 300 °C 2 h/H_2 300 °C 1h			0.050

a) $Pd(OAc)_2$ was impregnated on the untreated solid obtained from hydrolysis of $Ti(O\text{-}Pr^i)_4$.

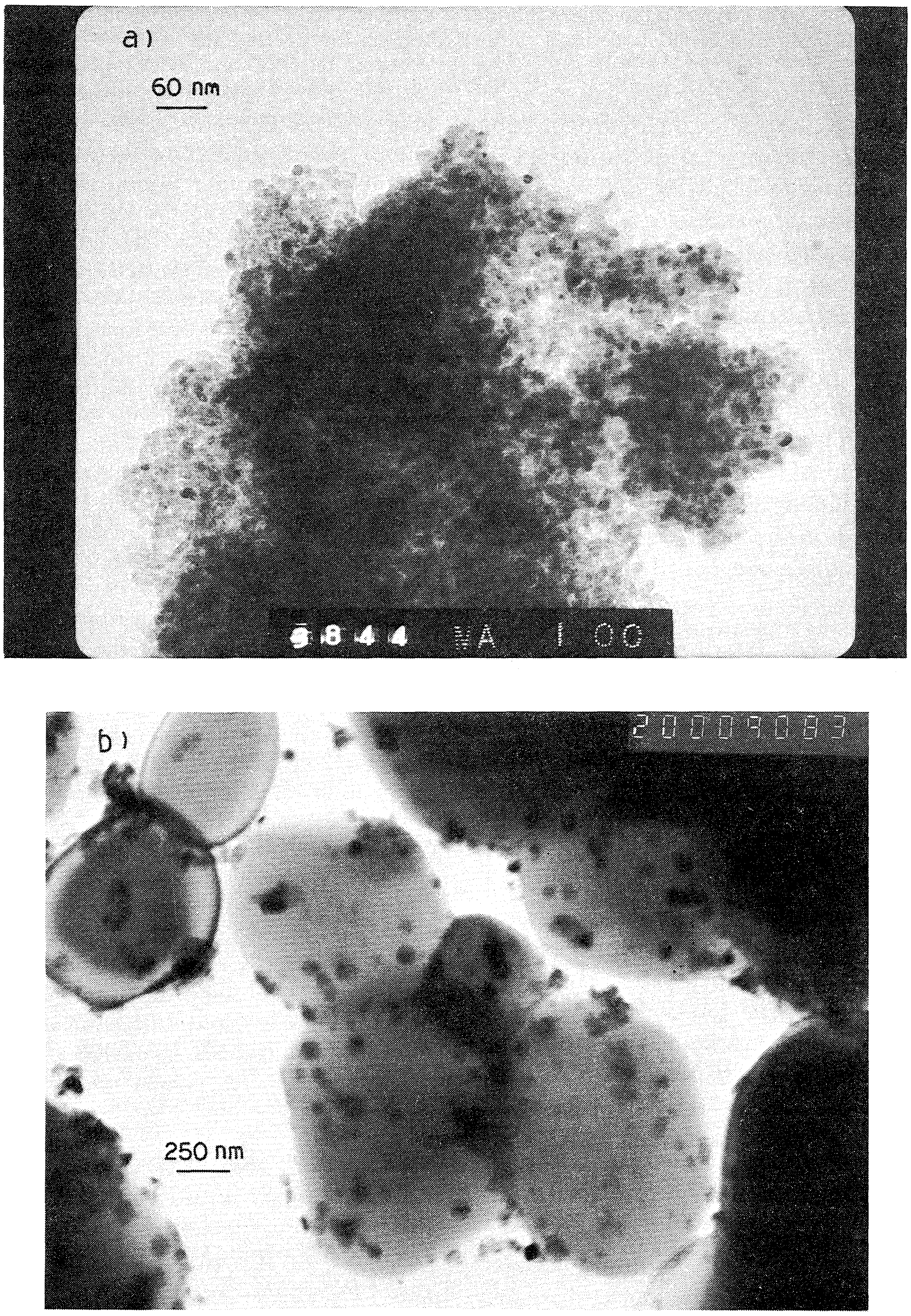


Fig. 1. TEM for a) coprecipitated catalyst A and b) impregnated catalyst B.

pared by coprecipitation of Pd(OAc)$_2$ and Ti(O-Pr^i)$_4$, achieved the highest surface area and the finest Pd particles among the three catalysts. Figure 1 shows TEM photographs for catalysts A and B. The distinction between the coprecipitated catalyst and the impregnated one is clearly seen. In the former, as a result of the preparation procedure, both Pd and the support were very fine particles and the two components were in such a well-mixed state that it is difficult to distinguish one from the other.

As shown in Table 1, a number of samples were prepared for each of the three catalysts with some variations in the conditions of heat treatment or in the preparation procedure to ensure reappearance by the preparation methods and the effects of the preparation conditions. Similar properties were generally achieved in the same group. For catalyst A, the amount of hydrogen adsorption apparently decreased after air treatment but no significant increase was seen in Pd particle size, as indicated by XRD.

The amount of hydrogen adsorption is presented as the ratio H$_{ad}$/Pd. Figure 2 gives a plot of H$_{ad}$/Pd vs. the reciprocal of average Pd particle size from XRD. The correlation between these two variables is approximately linear. The two air-treated samples of catalyst A deviated somewhat from the line. This is probably because during the air treatment the support crystal developed from its initial amorphous state and in that process some of the Pd might be wrapped inside the support. As a result, the adsorption capacity of the catalyst decreased without actual increase in Pd particle size. Though the proportional constant between the two amounts was not the same as that in the calculated equation[7] shown in the figure, the linear relationship shows that either of them can be used as a criterion to measure the relative difference of the catalysts. Here the value of H$_{ad}$/Pd is used to evaluate the specific activity of the catalysts.

Hydrogenation of CO. The main products of this reaction were methane and methanol. Under the present experimental conditions, the rate of methanol formation was affected significantly by equilibrium limitation as temperature increased beyond about 260 °C. Reactions were carried out mainly at 230 °C. Methanol production increased in the initial period of about two or three hours and then maintained a constant rate. Methane production deviated only slightly with time. Specific activities after reaching steady state are shown in Fig. 3 in terms of TOF (Turnover Frequency) based on hydrogen adsorption. Specific activity of the catalysts increased in the order C<B<A and this trend was especially remarkable for methanol formation. All the samples of catalyst A exhibited very similar activity and selectivity to each other and the production rate for methanol reached about 9 mmol/(g-Pd · h), which is quite high in comparison with the reported values for methanol synthesis on Pd catalysts at normal pressure.[1,8] However, catalyst C produced almost no methanol under the same conditions.

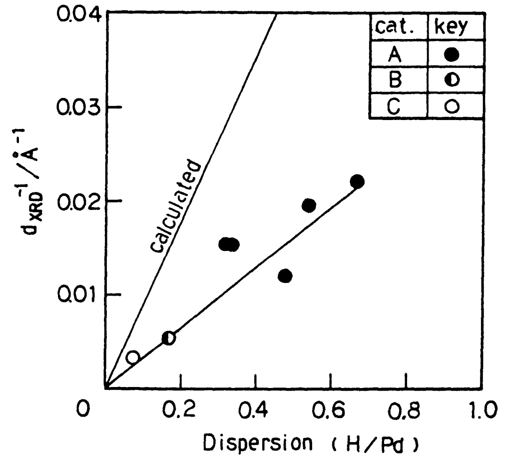


Fig. 2. Reciprocal of Pd particle diameter from XRD vs. Pd dispersion from hydrogen adsorption.

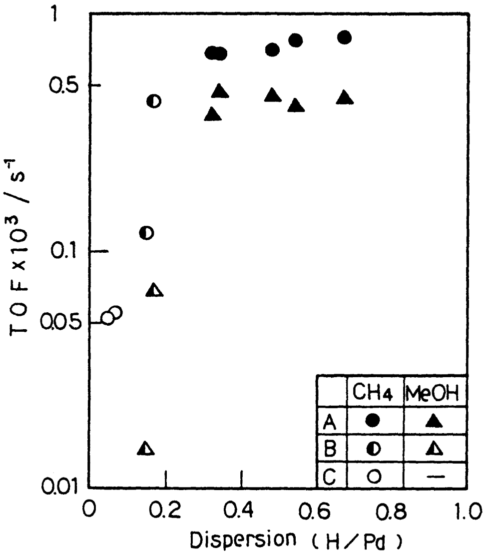


Fig. 3. Specific activity for formation of methane and methanol in the hydrogenation of CO: 1 atm, 230 °C, CO : H$_2$=1 : 4.

Hydrogenation of Acrylaldehyde (CH$_2$=CH-CHO) and Propionaldehyde (CH$_3$CH$_2$CHO). Acrylaldehyde is the simplest unsaturated aldehyde containing two kinds of double bonds—a C=C bond and a C=O bond. When hydrogenation of this compound was carried out at increasing temperature, at first the C=C bond was hydrogenated at comparatively low temperature and formed propionaldehyde. Then the second step of hydrogenating the formyl group took place at elevated temperature to produce 1-propanol. Catalyst A was found to be the only one on which the second step for 1-propanol formation occurred without completion of the first step. However, in the same temperature regime, though the hydrogenation of acrylaldehyde to propionaldehyde proceeded quite rapidly on catalysts B and C the resulting saturated aldehyde was not hydrogenated in spite of the completion of the first step.

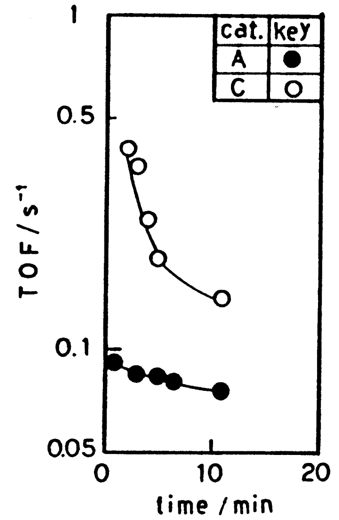


Fig. 4. Time dependence of activity for propionaldehyde formation in the hydrogenation of acrylaldehyde: acrylaldehyde 0.42%, H_2 33%, He 66.5%, 80 °C.

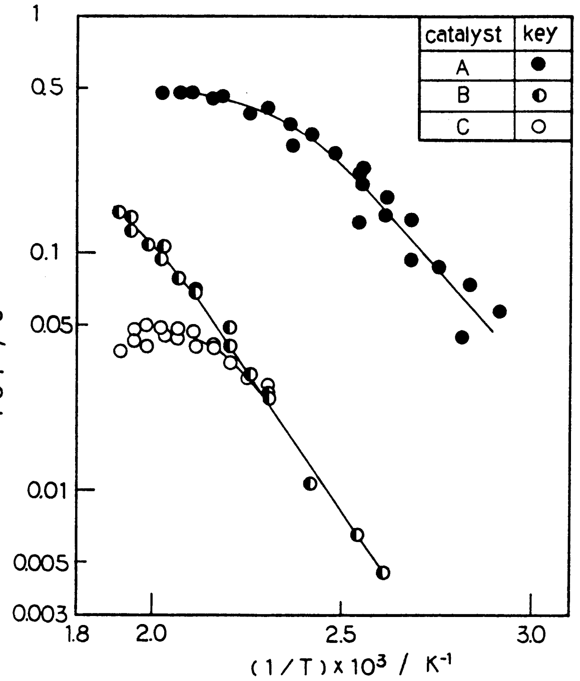


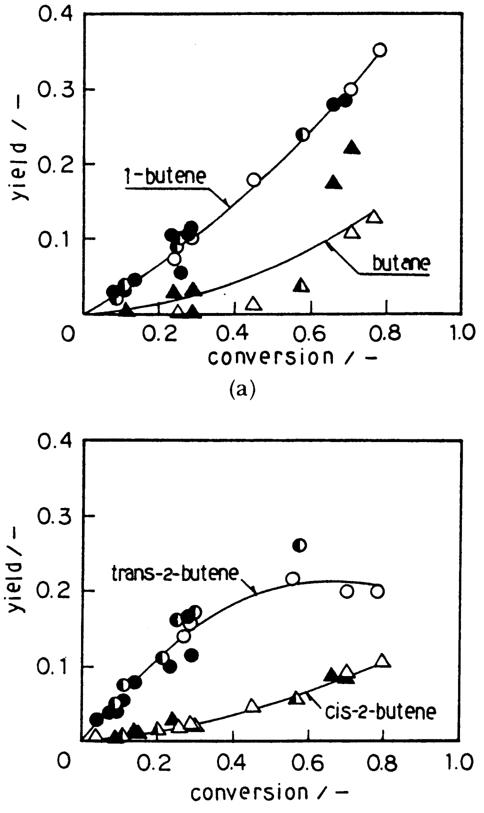
Fig. 5. Specific activity for 1-propanol formation in the hydrogenation of propionaldehyde: propionaldehyde 0.015%, H_2 33%, He 67%, 80 °C.

Figure 4 shows the time dependence of the turnover frequency obtained at 80 °C for catalysts A and C. In these experiments the total conversion was kept less than 10%. Under these conditions only propionaldehyde was produced and no 1-propanol was detected. The initial activity of catalyst C was about four times higher than that of catalyst A, when compared in terms of TOF.

However, in contrast to the C=C bond in acrylaldehyde, hydrogenation of the C=O bond in the formyl group was found to be quite different. In this case the relative activity of the catalysts showed a similar trend to that in the CO hydrogenation, with catalyst A being the most active one. Figure 5 shows the results from the reaction using propionaldehyde as the reactant. The figure is plotted as the temperature dependence of the production rate of 1-propanol. The activity of catalyst A was about one magnitude higher than that of the other two impregnated catalysts. The apparent slowness in increase of production rate observed in the high temperature region was due to the decomposition of the alcohol formed.

Hydrogenation of 1,4-Butadiene and Ethylene. Products of the hydrogenation of 1,4-butadiene included 1-butene, *trans*- and *cis*-2-butene and butane. Selectivities for the products are shown in Fig. 6, corresponding to the total conversion. All the catalysts had nearly the same selectivity and the general features of the product distribution were also consistent with those previously reported for Pd catalyst.[9] Among the products, *cis*-2-butene was produced only in a small amount. The fraction of butane was very low at small conversion but increased with the conversion, indicating that this product was a secondary product from successive hydrogenation of the butenes formed.

Remarkable differences in catalytic activity among the three catalysts were also observed in this reaction.



(a)

(b)

Fig. 6. Product distribution in the hydrogenation of 1,4-butadiene. ●▲ catalyst A, ◐▲ catalyst B, ○△ catalyst C.

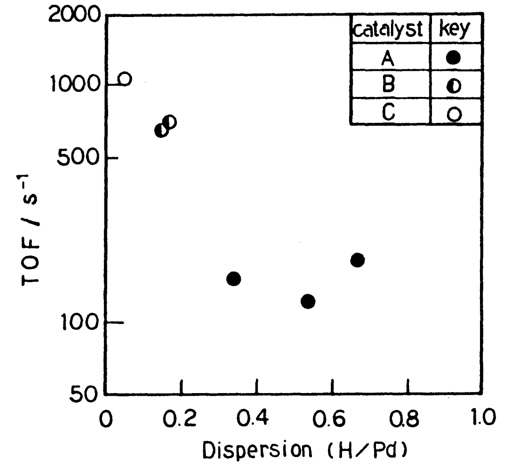


Fig. 7. Specific activity of catalysts in the hydrogenation of 1,4-butadiene: 1,4-C_4H_6 5%, H_2 95%, 80 °C.

Figure 7 gives a comparison of the initial activity of the catalysts, which was in the order C>B>A, with the most poorly dispersed catalyst being the most active one. This trend is similar to the results for hydrogenation of acrylaldehyde to propionaldehyde but contrary to those for hydrogenation of CO and propionaldehyde.

Hydrogenation of ethylene was carried out in a similar way. In this reaction, catalyst C seemed to be the most active one but the difference among the catalysts was not so strong as was observed in the other reactions. Average values of TOF for each catalyst are given in Table 2, together with the results obtained in the other reactions.

Discussion

The preparation methods used in this study gave Pd/TiO$_2$ catalysts showing quite different catalytic behavior from one another. Table 2 gives a summary of the reaction results. Activities were compared in terms of TOF based on hydrogen adsorption capacity. In the hydrogenation of CO, both the total activity and the individual activities for formation of CH_4 and CH_3OH were in the order of A>B>C. The well-dispersed catalyst A in particular was much more active than the other two. The same trend was observed in the hydrogenation of the C=O double bond in an formyl group. However, with the C=C double bonds the activity order of the catalysts was reversed. For the hydrogenation of ethylene, the simplest olefin, the difference in TOF among the three catalysts was not very remarkable. But in the hydrogenation of a C=C bond which was conjugated with another C=C or C=O bond, as in butadiene or in acrylaldehyde, a catalyst with higher dispersion showed lower activity.

In interpreting the difference in the activity of the catalysts, the concept of ensemble effect as having been mentioned above does not seem to be applicable to our case. This concept places stress on the differences in support properties, but in the present study, the two catalysts B and C, for which the same particles of TiO$_2$ were used as support, also showed quite different activities in the reactions. Here, it might be more useful to study the reaction results in relation to the nature of the different reactants.

In the five reactions examined, as listed in Table 2, the activity order of the catalysts observed in the hydrogenation of CO and propionaldehyde showed a contrary trend to that observed in the other reactions. By looking at the reactants, one can find some significantly different features between the first two and the other three. In carbon monoxide and a formyl group, the oxygen atom inclines to draw the electron because of its large electronegativity and thereby makes the molecule of CO or the CO bond of the aldehyde less electron-donative. In the case of an olefin, however, the C=C bond is usually electronically rich with its π-electron and has a tendency toward electron donation. This electron-rich state becomes stronger in a conjugated compound, where overlapping of the π-electron orbitals causes higher electron density on the molecule. Such different properties of the reactants are expected to bring about different patterns in their ways of interactions with the catalyst. Changes in the work-function of a metal when a compound is adsorbed on it provides one way of indicating the electronic interaction between the adsorbent and the metal. According to previous reports, adsorption of CO on Pd surface causes a positive shift in the work-function of Pd of 0.82 eV[10] while with adsorption of ethylene the work-function of Pd shifts about 0.8 eV negatively.[11] Thus with adsorption of CO, the electron transfers from Pd to CO, but with ethylene the electron transfer occurs in the opposite direction. It has been found for

Table 2. Average Activities of Catalysts A, B, and C

Reactions		T/°C	TOF/s^{-1}		
			A	B	C
Hydrogenation of CO	methane	230	7.3×10^{-4}	2.8×10^{-4}	5.5×10^{-5}
	methanol		4.3×10^{-4}	4.0×10^{-5}	0
Hydrogenation of propionaldehyde		80	1.6×10^{-1}	4.5×10^{-3}	4.5×10^{-3}
Hydrogenation of ethylene		80	380	500	580
Hydrogenation of C=C bond in acrylaldehyde		80	0.09		0.4
Hydrogenation of 1,4-butadiene		80	150	680	1050

Pt, one of the metals which show very similar properties to those of Pd, that the work-function of a Pt surface shifted 0.2 eV positively with adsorption of CO in contrast to the negative shifts of 0.8 eV and 1.6 eV with adsorption of ethylene and butadiene, respectively.12) This further indicates that donation of π-electron to the metal occurs to a larger extent on the conjugated diene than on ethylene. In corresponding to the relative extent of charge transfer on CO, ethylene and butadiene, our results showed that dependence of catalytic activity on Pd dispersion varied in reactions of these compounds. Activity for the hydrogenation of CO increased with increase in Pd dispersion. For the hydrogenation of ethylene, activity decreased slightly with the increase in Pd dispersion and in the reaction of 1,4-butadiene this decrease was much more obvious. As for the other two reactions of propionaldehyde and acrylaldehyde, the former behaved similarly to carbon monoxide while the latter was rather near to 1,4-butadiene as expected from the conjugating system composed of the C=C double bond and the aldehyde group in this molecule.

Pd with higher dispersion showed higher activity in the hydrogenation of electron-attractive compounds while in the hydrogenation of the electronically donative olefin bonds, Pd with lower dispersion was more active. These facts inversely suggest some changes in the electronic state of Pd, depending on its dispersed state on the support. According to the many studies of the hydrogenation of CO on Pd catalysts, it is known that bulk Pd metal is rather inactive in spite of its CO adsorption capacity.7,13) Previous study14) of a Pd alloy catalyst has shown that its catalytic activity was effectively increased after the alloy catalyst was treated in air to produce an oxidative state of Pd. These results indicated that the reaction of CO is favored by the oxidative state of Pd. In relation to these reported facts, the coprecipitated catalysts prepared in the present work are thought to be in a more oxidative state than Pd on the other catalysts.

The catalytic properties of supported metal catalysts may be affected by various factors and the situations are usually very complicated, making it difficult to determine the true state of the metal-support interaction. In this paper the experimental results obtained in the present work were discussed in relation to knowledge from past research and an interpretation of the different behavior observed for catalysts prepared by different methods was suggested by considering the electronic properties of the reactants and their interaction with Pd. The most plausible reason for the differences among the catalysts is thought to be the strength of the interaction between Pd and the TiO_2 support. Stronger interaction is expected on a catalyst prepared by coprecipitation which possesses a very large interface between Pd and the support.

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