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Preparation and Characterization of a Resin-Supported Palladium Catalyst

Takayoshi UEMATSU,* Masao UMINO, Shogo SHIMAZU, Masatoshi MIURA, and Hidehisa HASHIMOTO
Department of Synthetic Chemistry, Faculty of Engineering, Chiba University, Yayoi-Cho, Chiba 260

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The process of the ligand release and the reduction of $[Pd(NH_3)_4]$-form sulfonic resin has been studied by chemical analysis, X-ray photoelectron spectroscopy and adsorption techniques. The removal of ammonia ligands remarkably increased with hydrogen treatment above 353 K, and was complete at around 393 K. It is suggested that the released ammonia partly transfers to $-SO_3^-$ groups to form $-SO_3NH_4$ groups as the reduction proceeds. The dispersion of the metal particles prepared by hydrogen reduction ranged from 0.11 to 0.31 depending on the loading concentration of the palladium cation. The metal particles are considered to be entrapped in the pores of the resin. The formation of cationic palladium sites by the low temperature reduction is also suggested.

During our study on the nature of active sites of polymer anchored complex catalysts, we found that the various types of active sites can be prepared on ion-exchange resins by varying the pretreatment methods of cation-form resins. Several reports have been focussed on the differences in the catalytic nature of the active sites prepared on commercialy available ion-exchange resins.[1–4] In our trial, starting from cation-form sulfonic resins, two different types of active sites were prepared on the resin,[5] one of which is active for the isomerization and the other for the hydrogenation of butenes.

In the present study, we tried to scrutinize the process of active site formation by ligand removal from $[Pd(NH_3)_4]$-form sulfonic resin. The active sites thus prepared on the resin are characterized by means of chemical analysis, X-ray photoelectron spectroscopy (XPS), and adsorption of CO, NH_3, and acetylene. The catalytic activity was tested over these sites for the hydrogenation of ethylene. Further detailed catalytic behavior will be reported in a succeeding paper.

Experimental

Tetraamminepalladium complex cation, $[Pb(NH_3)_4]^{2+}$, was supported on Na-form sulfonic resin, denoted as AMNa (Amberlyst-15, Room & Haas; surface area: 51.3 $m^2\,g^{-1}$; ion-exchange capacity for Na^+ ion: 4.02 $mmol\,g^{-1}$-Na-form dry resin) according to the following ion-exchange process, viz.,

$$\left\{\begin{array}{l}\text{-SO}_3\text{-Na}\\ \text{-SO}_3\text{-Na}\end{array}\right. + [Pd(NH_3)_4]^{2+} \longrightarrow \left\{\begin{array}{l}\text{-SO}_3\diagdown\\ \text{-SO}_3\diagup\end{array}\right.[Pd(NH_3)_4] + 2Na^+ \qquad (1)$$

Since the cation-exchange was carried out in an ammonical solution of $[Pd(NH_3)_4]Cl_2$, a small amount of Na^+ ions on $-SO_3^-$ groups were substituted for NH_4^+ ions. The resultant palladium-form resin, denoted as Pd-Comp/AMNa, was rinced with decationized water, and dried at 333 K for a week. The loading concentration of the palladium complex was determined by an atomic absorption method. For comparison, $[Pd(NH_3)_4]Cl_2$ was also loaded on silica gel (Tokai gel-50; surface area: 310 $m^2\,g^{-1}$) by a similar impregnation method which is denoted as Pd-Comp/SiO_2.

The adsorption of CO, NH_3, and C_2H_2 was studied by gravimetry using an electrobalance (Cahn model 2050 RG). The change in the oxidation states of the palladium due to hydrogen treatment was studied by a photoelectron spectrometer (Kratos XSAM 800) with Mg $K\alpha$ X-ray radiation. The catalytic activity was tested for the hydrogenation of ethylene in a closed circulating system.

Results and Discussion

The removal of ammonia ligands from Pd-Comp/AMNa (Pd: 0.08 $mmol\,g^{-1}$) during the pretreatment was firstly studied by chemical analysis for nitrogen. The result is given in Table 1. The contents of palladium and sulfur were constant within the experimental error, irrespective of the various reduction procedures applied. This indicates that the sulfonic groups are stable during the pretreatment.

The total nitrogen content, N(anal), decreased with increase in the reduction temperature. The initial nitrogen content obtained for a sample evacuated at room temperature, (No. 1), was considerably higher than that estimated from the stoichiometric ammonia coordination number, $NH_3/Pd=4$ for Pd-Comp/AMNa. This excess nitrogen is probably due to the presence of ammonium ions on $-SO_3^-$ groups formed during the ion-exchange process of the palladium complex in the ammonical solution as described above.

The thermal stability of this ammonium sulfonate was evidenced by the fact that no ammonia release was detected on heating NH_4-form resin up to 493 K under vacuum. Further, at room temperature, the total nitrogen content on the Pd-Comp/AMNa did not change after pumping for 3 h.

Thus, for the hydrogen-reduced Pd-Comp/AMNa,

Table 1. Chemical Analysis of Pretreated Palladium-Form Sulfonic Resin

	Treatment	Content/mmol g^{-1}					
		S	Pd	N(anal)	N(s)	N(Pd)	N(Pd)/Pd
1	Evac Room Temp	4.06	0.080	0.625	0.305	0.320	4.00
2	Evac 373 K 2 h H_2 353 K	3.96	0.082	0.568	0.305	0.263	3.21
3	Evac 373 K 2 h H_2 383 K	4.10	0.078	0.525	0.305	0.220	2.82
4	Evac 373 K 2 h H_2 393 K	4.00	0.082	0.506	0.305	0.201	2.45
5	Evac 373 K 2 h H_2 473 K (Flow)	3.99	0.082	0.418	0.305	0.113	1.38
6	HCHO-treat. 333 K	4.02	0.082	0.400	0.305	0.095	1.16

N(anal) is the total nitrogen by chemical analysis. N(s) and N(Pd) indicate the number of NH_4 on $-SO_3^-$ and NH_3 on the palladium, respectively. See text.

the amount of the ammonium ion originally bound to sulfonic groups was calculated as N(s)=0.305 mmol g^{-1} by substraction of the stoichiometrically coordinated ammonia ligands to the palladium, N(Pd)= 0.320 mmol g^{-1}, from the total ammonia which was given by nitrogen chemical analysis as N(anal)=0.625 mmol g^{-1} for Pd-Comp/AMNa evacuated at room temperature.

Since ammonium sulfonate is stable and N(s) was considered to be constant for all samples treated by H_2 below 493 K, the values of N(Pd) for the variously treated Pd-Comp/AMNa were determined, in turn, from the differences between N(anal) and N(s). The ammonia coordination number to the palladium, N(Pd)/Pd, was also calculated. These values are listed in Table 1.

The coordination number for Pd-Comp/AMNa (Pd: 0.08 mmol g^{-1}) decreased from 4 to 2.45 when the hydrogen treatment temperature was increased up to 393 K. The reduction at a higher temperature of 473 K (No. 5) led to a marked decrease in nitrogen content, N(anal), and only 0.113 mmol g^{-1} of ammonia ligand was left on the palladium. The reduction in the formaldehyde solution (No. 6) gave rise to a similar dramatic decrease in N(Pd) to 0.095 mmol g^{-1}. However, these values still correspond to the residual coordination number of N(Pd)/Pd=1.38 and 1.16 respectively.

The weight loss due to the ammonia release during pretreatment was also studied as shown in Fig. 1. The hydrogen treatment at 353 K was only sufficient to remove 10% of the ammonia from the palladium. The treatment at higher temperatures facilitated the ligand removal and 50% of ammonia release, NH_3(des), was attained at 433 K. It is noticeable that further elevation of the reduction temperature up to 453 K had no effect on the residual ammonia on the resin.

Figure 2 shows the effect of the hydrogen treatment on the oxidation state of the palladium studied by

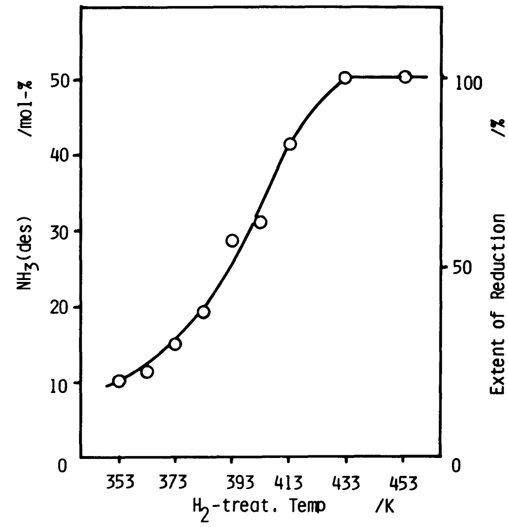

Fig. 1. Removal of ammonia ligand by H_2-treatment Pd-Comp/AMNa(Pd: 0.519 mmol g^{-1}): evacuated at 373 K for 2 h and subjected to hydrogen treatment for 1 h at $P(H_2)$=26.6 KPa.

XPS. Pd-Comp/AMNa (Pd: 0.519 mmol g^{-1}) was first evacuated in the preparation chamber over night at 1.33×10^{-6} Pa. The peak due to Pd^{2+} (3d-5/2) was detected at a binding energy B. E. of 339.2 eV, but gradually shifted to 337.2 eV on increasing the hydrogen treatment temperature up to 433 K. The latter peak was ascribed to palladium metal, Pd^0 (3d-5/2) on the sulfonic resin. The hydrogen treatment at 453 K appeared to complete the reduction of the palladium cations. Refluxing in a formaldehyde solution at 353 K seemed also to reduce them completely to the metal.

However, as shown in Table 1, the complete reduction with H_2 or formaldehyde did not necessarily result in the decrease in the total nitrogen to zero. The reason for this may well be explained in terms of "ammonia transfer" from the palladium to

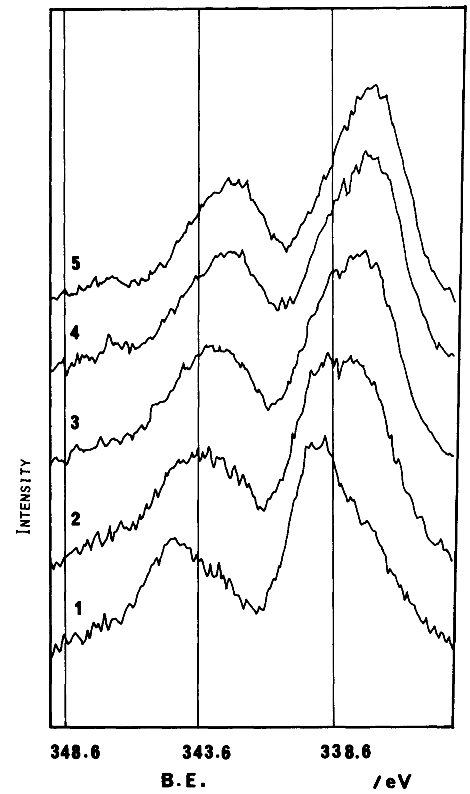

Fig. 2. XPS spectra for H_2-treated palladium-form sulfonic resin.
Sample: Pd-Comp/AMNa(Pd: 0.519 mmol g^{-1}). 1: evacuated at 353 K in the preparation chamber over night at 1.33×10^{-10} Pa, 2: H_2-treated at 358 K for 60 min after 1, 3: H_2-treated at 398 K for 20 min after 2, 4: H_2-treated 433 K for 20 min after 3, 5: H_2-treated at 453 K for 20 min after 4. The binding energy was referred to C(1s): 284.9 eV, Pd metal on Na-form sulfonic resin: 336.5 eV and Pd metal(Solid): 335.0 eV.

the sulfonic groups during the reduction; this was previously proposed in an analogous system of a palladium ammine complex cation on zeolites,[6] viz.,

$$\left.\begin{matrix}\text{-SO}_3\\\text{-SO}_3\end{matrix}\right\rangle[\text{Pd(NH}_3)_4] + \text{H}_2 \longrightarrow \left\{\begin{matrix}\text{-SO}_3\text{NH}_4\\\text{-SO}_3\text{NH}_4\end{matrix}\right. + \text{Pd}^\circ + 2\text{NH}_3 \qquad (2)$$

If this is the case, the extent of reduction is directly related to the removal of ammonia ligands from the palladium. As shown in Fig. 1 the weight loss due to the ammonia release was almost complete at 433 K, where 50% removal of ammonia from Pd-Comp/AMNa was attained. This suggests that Eq. 2 is also valid for Pd-Comp/AMNa and the 100% reduction was accomplished as indicated also by the XPS study. An Arrehenius plot for the ammonia release gave an activation energy of 74 KJ mol^{-1}.

Re-adsorption of ammonia was studied over the hydrogen treated Pd-Comp/AMNa (Pd: 0.519 mmol g^{-1}) and the result is shown in Fig. 3. After the hydrogen treatment at 353 K, the ammonia re-adsorption amounted to about NH_3(ad)/Pd=0.5. This value is close to that of ammonia previously removed, 0.4, during the hydrogen treatment. This suggests that the coordination and the release of ammonia are quite reversible over the samples treated at this low temperature region. However, after the treatment above 373 K the amount of ammonia re-adsorption decreased remarkably to give the ratio, NH_3(ad)=0.25. Thus, the ammonia was removed irreversibly when the Pd-Comp/AMNa was once reduced at high temperatures.

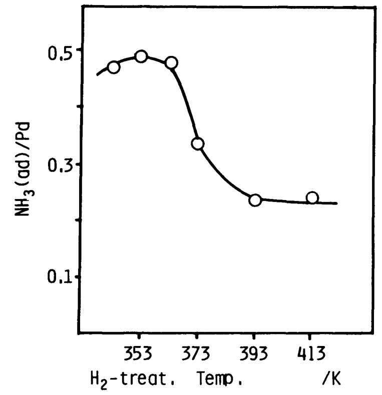

Fig. 3. Re-adsorption of NH_3 over H_2-treated palladium-form sulfonic resin
Pd-Comp/AMNa(Pd: 0.519 mmol g^{-1}) was evacuated at 373 K for 2 h and subjected to H_2-treatment for 1 h under $P(H_2)=26.6$ KPa. Adsorption: 303 K, $P(NH_3)=399$ Pa.

Carbon monoxide has been widely used as a probe to characterize catalytic sites of supported metal catalysts.[7,8] The effect of hydrogen treatment on CO adsorption are shown in Figs. 4 and 5. In the case of Pd-Comp/AMNa (Pd: 0.519 mol g^{-1}), the amount of adsorbed CO was increased on raising the hydrogen treatment temperature from 353 K to 393 K and reached a constant level of CO(ad)/Pd=0.28. The further elevation of temperature did not change the value.

Figure 5 shows similar results for Pd-Comp/AMNa with different palladium concentrations and for Pd-Comp/SiO_2. The temperature where the ratio, CO(ad)/Pd, attained constant values almost coincided with each other at about 393 K, irrespective of the different supports and different loading concentrations applied. Moreover, the amount of CO adsorbed on Pd-Comp/SiO_2 decreased little on further elevation of the treatment temperature up to 673 K.

A similar trend was obtained for the adsorption of acetylene. Figure 6 shows that the amount of adsorption increased with the hydrogen treatment temperature up to 403 K and reached a constant value, which may be related to the completion of the reduction.

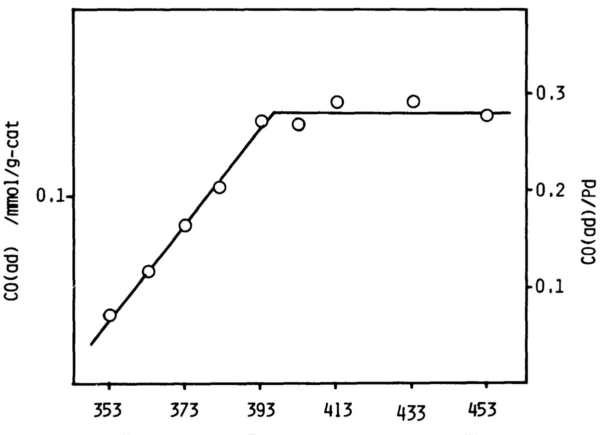

Fig. 4. Effect of H_2-treatment on CO adsorption Pd-Comp/AMNa (Pd: 0.519 mmol g^{-1}) was evacuated at 373 K for 2 h and subjected to H_2-treatment for 1 h. Adsorption of CO at 303 K, under P(CO)=399 Pa.

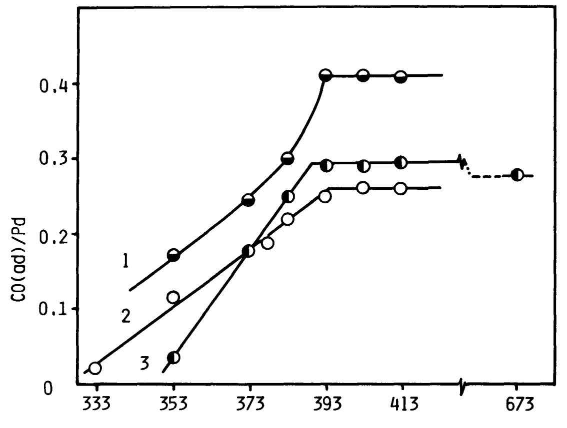

Fig. 5. Effect of CO adsorption on palladium-form sulfonic resin and silica supported palladium.
Samples were evacuated at 373 K for 2 h and subjected to H_2 hydrogen treatment at T K for 1 h. Adsorption was carried out at 273 K at P(CO)=399 Pa. 1: Pd-Comp/AMNa (Pd: 0.0904 mmol g^{-1}). 2: Pd-Comp/AMNa (Pd: 0.12 mmol g^{-1}). 3: Pd-Comp/SiO_2. (Pd: 1.00 mmol g^{-1}).

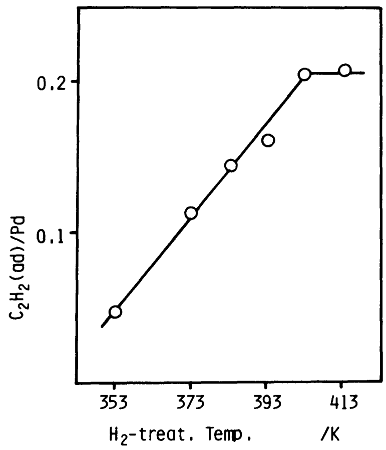

Fig. 6. Effect of H_2-treatment on C_2H_2 adsorption Pd-Comp/AMNa (Pd: 0.519 mmol g^{-1}) was evacuated at 373 K for 2 h and subjected to H_2-treatment at T K for 1 h.

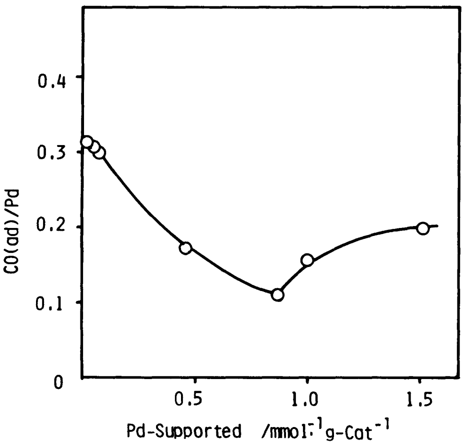

Fig. 7. Effects of palladium loading concentration on CO adsorption.
Pd-Comp/AMNa (Pd: 0.519 mmol g^{-1}) was evacuated at 373 K for 2 h and subjected to H_2 treatment at 403 K for 1 h. Adsorption at 273 K at P(CO)=399 KPa.

If the reduction of palladium was once completed, the number of CO adsorption sites would not increase any more by further elevation of the reduction temperature. Moreover, the values of CO(ad)/Pd would decrease if the sintering proceeded. However, the observed values were almost constant from 393 to 453 K for Pd-Comp/AMNa (Pd: 0.519 mmol g^{-1}) and to 673 K for Pd-Comp/SiO_2, and thus, it may be said that the palladium metal particles are highly stable over the widespread temperature range.

In view of the different behavior between ammonia and CO adsorption in Figs. 3, 4, and 5, the adsorption sites produced by the treatments can be ascribed respectively to palladium cations with unsaturated ligands and the metal sites. The isomerization of butenes takes place over the cation site,[5] while the adsorption of CO and acetylene (Fig. 6) can be attributed to the metal sites formed by the high temperature reduction according to Eq. 2.

The effect of the loading concentration on the dispersion of palladium is given in Fig. 7. In this case, the palladium cations were completely reduced to the metal by hydrogen treatment at 403 K. The dispersion of the metal particles is defined by D=Pd(surface)/Pd(total),[9] where Pd(surface) was determined by CO adsorption. The average particle sizes were estimated from the equation, d=1.23/D nm.[10] The maximum dispersion, 0.31, and the minimum, 0.11 correspond respectively to d=3.97 and 11.2 nm. The formation of these fine particles may be facilitated by the retardation of the diffusion and the sintering of palladium by anchoring on $-SO_3^-$ groups.

Table 2. Dispersion and Particle Size of Palladium Metal Prepared by Reduction with Formaldehyde

	Sample	Pd loaded /mmol g^{-1}	Dispersion D=CO/Pd	Diameter d/nm
1	Pd-Comp/AMNa(F)	0.090	0.075	16.5
2	Pd-Comp/AMNa(F)	1.11	0.020	62.0

Pd-Comp/AMNa(F): Pd-Comp/AMNa was reduced by refluxing in a formaldehyde solution at 358 K for 5 min.

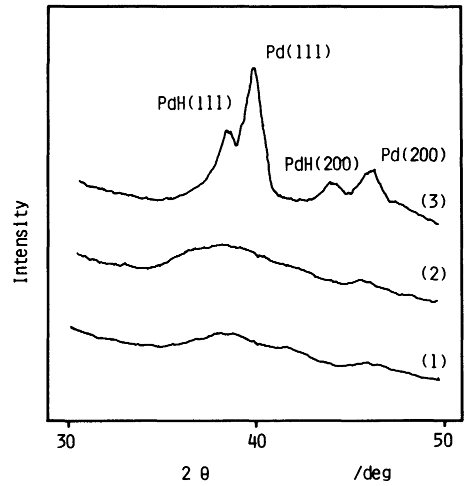

Fig. 8. XRD spectra for palladium-form sulfonic resin Pd-Comp/AMNa(Pd: 0.519 mmol g^{-1}).
1: H_2-treated at 353 K. 2: H_2-treated at 393 K. 3: formaldehyde treated at 358 K.

The mean pore diameter measured by the mercury penetration method was 24.8 nm for the support AMNa which agreed well with the reported value of 25.6 nm.[11] The total amount of palladium complex contained in a pore can be estimated from the loading concentration and the BET surface area. A pore of average diameter of 24.8 nm has a surface area of 1.93×10^3 nm^2 where the palladium cations anchored are 1.98×10^3 and 1.25×10^4, respectively for Pd-Comp/AMNa (Pd: 0.08 mmol g^{-1}) and Pd-Comp/AMNa (Pd: 0.519 mmol g^{-1}).

Based on a cubo-octahedral crystal model,[12] the expected dispersions of the metal particles in the pore was estimated to be about D=0.32 and 0.19 which are very close respectively to the observed values of 0.31 and 0.18 in Fig. 7. This fact suggests that the particle size of the metal palladium was controlled by entrapment within each pore in the resin.

While the reduction by formaldehyde resulted in a smaller dispersion as given in Table 2. A highly loaded Pd-Comp/AMNa (Pd: 1.1 mmol g^{-1}) gave larger particles than that for the mean pore size. They might grown outside of the pore due to the increase in the sintering probability and the particle sizes.

The X-ray diffraction spectra for a formaldehyde-treated Pd-Comp/AMNa(F) in Fig. 8 shows clear patterns of palladium metal. The crystallite diameter obtained by Scherre's equation was about 12 nm. The formation of palladium hydride, $PdH_{0.706}$ was also indicated in the spectra.

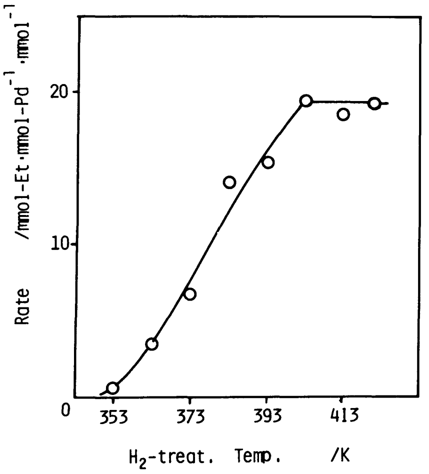

Fig. 9. Catalytic activity for the hydrogenation of ethylene over H_2-treated Pd-Comp/AMNa.
Pd-Comp/AMNa (Pd: 0.519 mmol g^{-1}): evacuated at 373 K for 2 h and subjected to H_2-treatment at T K for 1 h. The reaction was carried out at 313 K with 1 : 1 mixture of C_2H_4 and H_2.

The evidence of the formation of catalytic sites due to metallic palladium is given in Fig. 9. The catalytic activity for the hydrogenation of ethylene changed almost in parallel with the numbers of the metal sites for CO and acetylene adsorption sites (Figs. 4, 5, and 6). Thus, it may be conclusively said that the partial reduction takes place gradually from low temperature hydrogen treatment and the complete reduction is accomplished above 393 K where the catalytic activity also the reached a constant level. The results by XPS study also supports this observation.

Conclusion

Fine metal palladium can be prepared on a sulfonic resin by the reduction of $[Pd(NH_3)_4]$-form resin. The particle size can be controlled by changing the loading concentration and the reducing condition. The metal particles may be formed in the pores by the effect of the entrapment, when the loading concentration was kept low. The low temperature treatment may also produce cationic sites with vacant ligands by removing the ammonia ligands.

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