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A study on the dispersion and catalytic activity of gamma alumina-supported palladium catalysts

Nabin K. Nag

Engelhard Corporation, 23800 Mercantile Road, Beachwood, OH 44122, USA

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Electron spectroscopy for chemical analysis (ESCA) and carbon monoxide adsorption techniques have been applied to study the percent exposed (i.e., dispersion) and Pd deposition in the pores of highly porous gamma alumina-supported Pd catalysts. A correlation has been found between Pd dispersion and its extent of penetration into the pores: more edge-coated catalysts are less dispersed. The dispersion of Pd is controlled by a carrier–catalyst interaction that originates in part from electron transfer from the support to the supported Pd. This electronic interaction is demonstrated by the broadening of the ESCA peaks. The activity of the catalysts, measured by the hydrogenation of nitrobenzene to aniline, is dependent on the dispersion of palladium.

Keywords: ESCA; CO adsorption; dispersion; Pd deposition; Pd / Al_2O_3

1. Introduction

The effect of high surface-area refractory oxide catalyst supports, such as alumina, on active catalytic species is basically two-fold: first, it disperses the active species (generally, a metal, a metal oxide or sulfide), thus exposing a large fraction of the supported material to the reacting molecules; and second, it often modifies the electronic properties of the supported species. These interactions often generate catalysts with desired activity and selectivity.

The phenomenon of metal–support interaction and its effect on the catalytic properties of supported catalysts have been studied extensively [1–6]. Dramatic effects of this interaction on the chemisorptive and catalytic properties have been observed. Most of the industrial catalysts contain a small amount of the active components carried on high surface-area supports such as alumina, activated carbon etc. The choice of the support depends on several factors including its stability in the reaction medium, the nature of its porous structure, surface area, acidity and others. Right choice of the support is crucial in designing a supported catalyst with desired activity and selectivity. Therefore, it is important to understand the nature and origin of carrier–catalyst interaction to design catalysts for specific applications.

In the present work, a series of alumina-supported palladium catalysts have been investigated by ESCA, CO adsorption, and by other common physical characterization methods. The purpose has been to understand the dispersion mechanism of Pd on gamma alumina supports with widely varying physical properties, and to relate the results to the activity of these catalysts for a model hydrogenation reaction.

2. Experimental

The catalysts were prepared by adsorbing suitable Pd ions on alumina powders followed by reduction. The Pd contents of the finished catalysts were determined by atomic adsorption spectroscopy.

A Surface Science ESCA machine (model SSX-100) using Al K_α monochromatic X-rays (1486 eV) was used to generate the spectra. An electron floodgun (2 eV) was used to compensate for any differential charging due to the insulating properties of the supports. The C_{1s} (BE: 284.6 eV) line, arising from carbon impurities, was taken as the standard for correcting the binding energies. Quantitative analyses of ESCA data were performed with the intensities of the peaks using Scofield sensitivity factors [7].

A dynamic flow technique was used to measure carbon monoxide uptake. In a typical experiment, a known amount of catalyst was reduced in a flow of hydrogen at 325°C for 2 h, followed by flushing with argon. The system was cooled down to 25°C in argon and then CO was swept over the catalyst bed. The uptake of CO was estimated, from an average of two experiments, by analyzing the effluent gas with a thermal conductivity detector.

Pore size distribution was measured by the mercury penetration method, and the BET surface area by adsorbing nitrogen at liquid nitrogen temperatures. Average Pd crystallite size was measured by the X-ray line broadening method [8].

The activities of the catalysts for the slurry-phase hydrogenation of nitrobenzene to aniline were measured as the rate of hydrogen consumption per gram of Pd at 25°C.

3. Results

The Pd contents and the physical properties of the catalysts are given in table 1. It is observed that surface area, pore volume and Pd crystallite size vary widely among the catalysts. The variations in surface area and pore volume are ascribed to various sources and pretreatment procedures of the support alumina. However, the wide variation in Pd crystallite size, in spite of nearly similar catalyst preparation techniques having been applied, is indicative of some specific interaction

Table 1
Physical properties of the catalysts

Catalyst No.	Alumina type[a]	Preparation and reduction methods	wt% Pd	Pd cryst. size[b] (Å)	Surf. area[c] (m^2/g)	Pore vol.[d] (ml/g)
1	AP-1	prep. method-1/red. meth-1	5.4	100	100	0.52
2	AP-2	prep.-1/red.-1	5.6	100	97	0.29
3	AP-3	prep.-1/red.-1	5	80	97	0.60
4	AP-4	prep.-1/red.-1	5.2	190	64	0.93
5	AP-5	prep.-1/red.-1	5	80	243	2.20
6	AP-5	prep.-1/red.-2	4.8	110	220	2.00
7	AP-5	prep.-1/red.-3	4.9	75	220	2.00
8	AP-5	prep.-2/red.-1	4.9	100	253	2.20
9	AP-5	prep.-3/red.-1	4.5	270	211	1.90
10	AP-5	prep.-4/red.-1	4.9	250	227	2.30

[a] AP-1,2 etc. indicate: alumina powder from source 1,2 etc.
[b] Pd crystallite size measured by X-ray line broadening method.
[c] Surface area by BET method.
[d] Pore size distribution by mercury penetration method using 130° contact angle.

between the supports and Pd. This specificity probably arises from the unique nature of the supports.

A representative ESCA spectrum is shown in fig. 1. It is observed that the peaks are quite broad. By using a deconvolution program each peak can be resolved into three components, and the central peak has the highest intensity. The resolution of the peaks into multiple components is attributed to the presence of Pd species

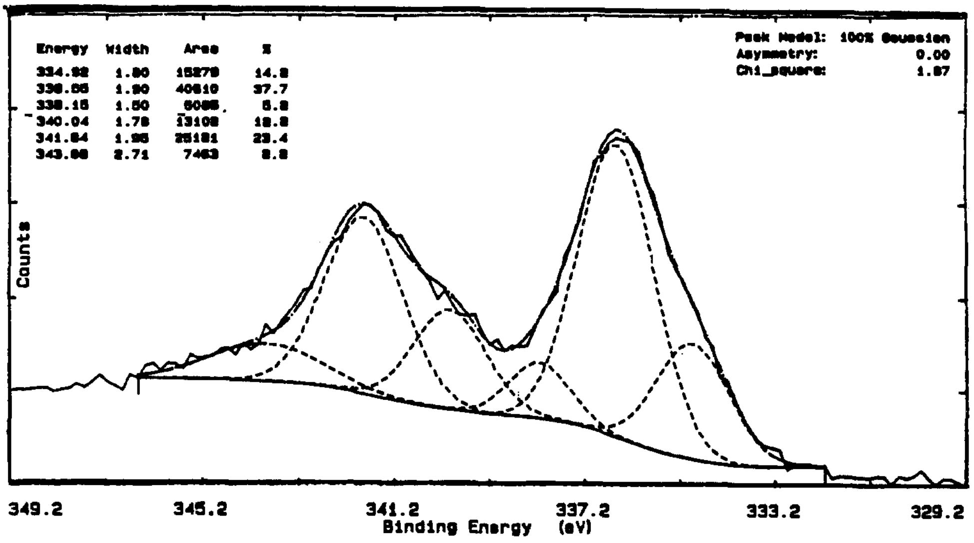


Fig. 1. A representative ESCA spectrum of Pd in 5% Pd on gamma alumina. Note the deconvolution of the peaks.

with various oxidation states. Although the catalysts were all reduced, no special care was taken to avoid exposure to air either during storing or during ESCA sample preparation. For subsequent analyses based on binding energy and peak intensity this central component of $Pd_{3d_{5/2}}$ has been used in this work. The BE of this component varies in the range 332.9–336.5 eV and the full width at half-maximum (FWHM) in the range 1.9–2.8 eV. These ranges are quite broad and their significance will be discussed in the upcoming sections.

Metal percent exposed (to be called "dispersion") has been calculated from CO uptake by assuming a 1 : 1 stoichiometry of CO adsorption on Pd. Pd dispersion, measured in this manner, is found to vary between 19 and 47%. This does not give a clear picture of how Pd is distributed across the length of the pores. However, by comparing the CO adsorption data with the surface concentration of Pd, as measured by ESCA, one can get a good idea about it. In view of this, ESCA Pd : Al ratios have been plotted as a function of Pd dispersion in fig. 2. It is observed that Pd enrichment of the pore mouths, as indicated by higher Pd : Al ratio, decreases as the dispersion of Pd increases. This decrease is quite sharp at the lowest region of Pd dispersion, and levels off at the highest dispersion region.

The correlations among pore volume, surface area and Pd dispersion are shown in fig. 3. The effect of BE of Pd ($3d_{5/2}$) on Pd dispersion is shown in fig. 4, and that of Pd dispersion on the FWHM is demonstrated in fig. 5. The correlation between the FWHM of Pd ESCA peaks and the BE is shown in fig. 6.

The correlations among the hydrogenation activity of the catalysts and Pd dispersion and Pd : Al ratio, as measured by ESCA, are displayed in fig. 7. It is observed that the hydrogenation activity increases as a function of Pd dispersion, whereas it declines sharply as the Pd : Al ratio increases.

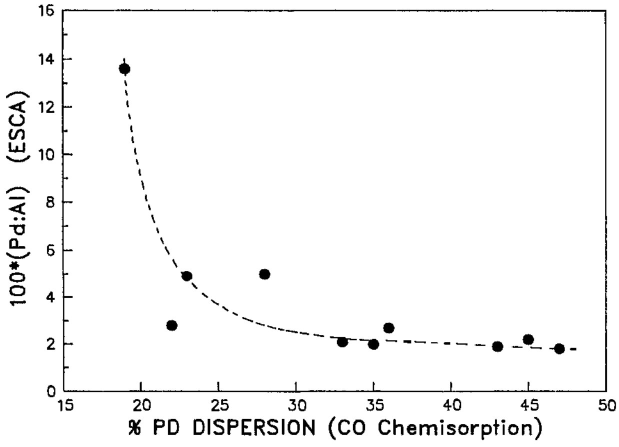


Fig. 2. Correlation between Pd : Al atomic ratio (ESCA) and Pd dispersion as obtained by CO adsorption.

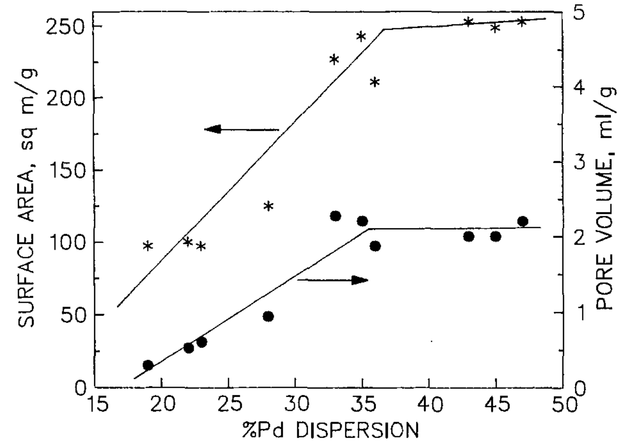


Fig. 3. Correlations among Pd dispersion, pore volume and surface area of the catalysts.

4. Discussion

The catalysts are all based on gamma alumina and prepared by very similar procedures. They were reduced by three different methods (see table 1). However, the supports originated from different commercial sources, and as seen in table 1, they have widely different physical properties.

The combined effect of these varying physical characteristics associated with the different aluminas leads to the widely varying dispersion, metal deposition profiles on the support and hydrogenation activities of the supported metal.

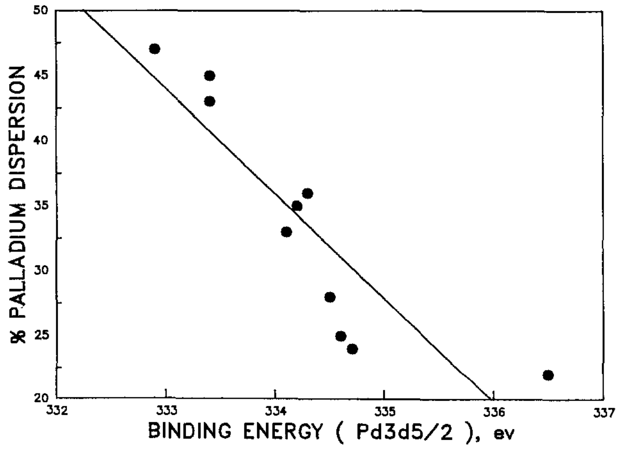


Fig. 4. Correlation between Pd binding energy and Pd dispersion.

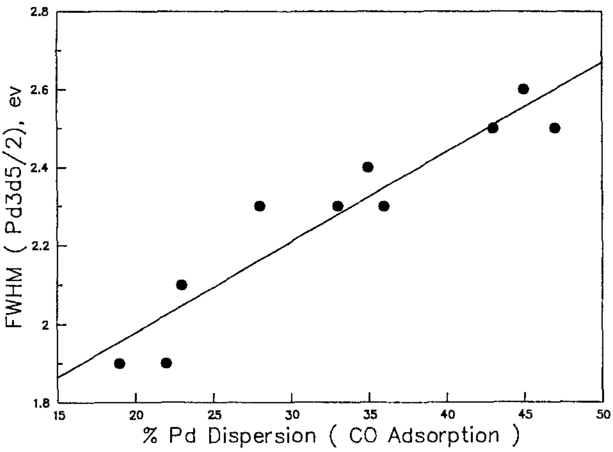
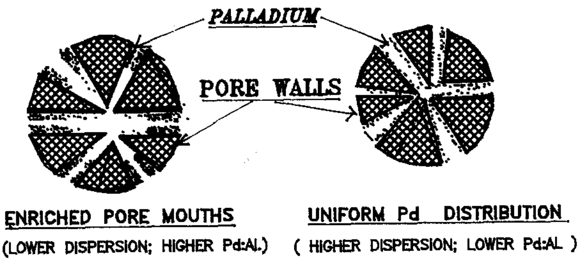


Fig. 5. Correlation between Pd dispersion and FWHM.

4.1. METAL DISPERSION AND DISTRIBUTION

Fig. 2 demonstrates a wide variation in the dispersion of Pd as well as the ESCA Pd : Al atomic ratio. The Pd : Al atomic ratio decreases very sharply (from 0.14 to 0.02) as Pd dispersion increases from 19 to 27%, and then remains practically unaffected by further increase in the dispersion. A higher Pd : Al ratio, as measured by ESCA, is indicative of enrichment of the support pore mouths by Pd, as opposed to more uniform deposition of metal throughout the whole length of the pores. The two types of metal deposition in the pores are schematically represented as follows:



It is perceived that as the depth of Pd penetration into the pores increases, the dispersion increases due to greater extent of spreading of Pd on the walls. This allows a larger fraction of the metal to be titrated by CO, resulting in higher metal dispersion. In this situation, there is no physical restriction for CO to access the metal lying inside the deep recess of the pores as long as the pore mouths are not completely blocked. The situation with ESCA, however, is different. When most of the metal is located near the pore mouths, the photoelectrons emanating from almost

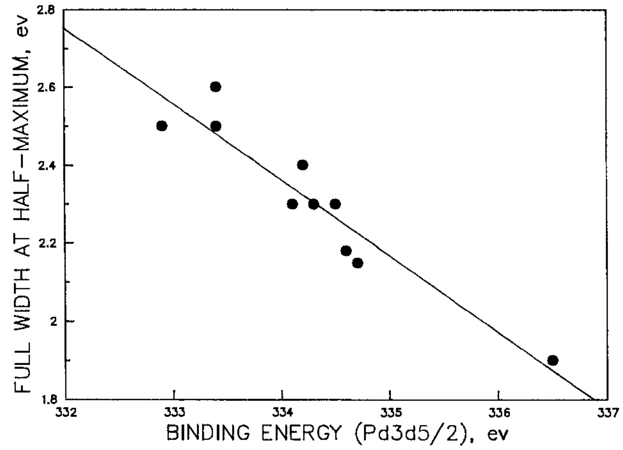


Fig. 6. Correlation between Pd binding energy and FWHM.

all the Pd atoms are detected by ESCA because the depth of the metal layer in the pore mouths is within the mean free path of the electrons. However, as the metal moves deeper and deeper inside the pores, the intensity of the photoelectrons decreases rapidly (an exponentially decreasing relationship exists between the depth of origin and intensity of the photoelectrons). Eventually a situation arises when the metal, lying beyond a certain depth, is no longer detected simply because the electrons emitted from it do not reach the detector. This explains the inverse relationship between dispersion and ESCA Pd : Al ratio, as depicted in fig. 2.

From the results discussed above it is concluded that Pd penetration into the pores of micron-size alumina particles is dependent on the porous structure of the alumina. The combined ESCA and CO adsorption work, as applied and analyzed in this work, offers a means of discriminating between edge- versus uniformly-coated powder catalysts. This task is often not straightforward and easy.

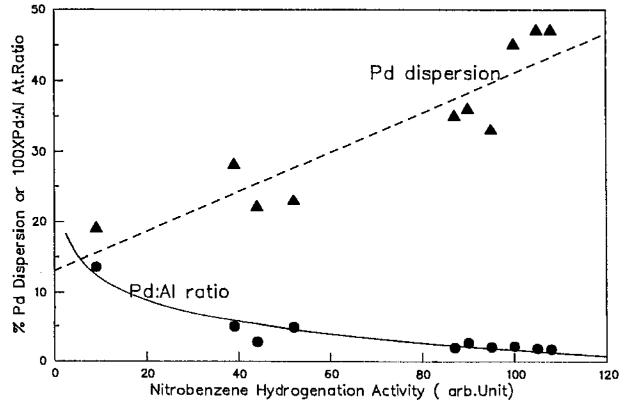


Fig. 7. Correlations among hydrogenation activity, Pd dispersion and Pd : Al ratio (ESCA)

The important question now arises: What are the factors that dictate the state of Pd as regards its dispersion and disposition on the support? An answer is sought in the following sections.

4.2. DISPERSION VERSUS SURFACE AREA AND PORE VOLUME OF SUPPORT

Of all the physical parameters listed in table 1, pore volume and surface area are the only ones that show some reasonable correlation with Pd dispersion. The supports were so chosen that there was a wide variation in surface areas and pore volumes (60–250 m^2/g and 0.3–2.3 ml/g respectively). The correlations among dispersion, surface area and pore volume are shown in fig. 3. It is observed that the dispersion increases as a function of surface area as well as pore volume. These correlations indicate that more porous and larger surface-area supports allow easier access of the Pd salt to deeper regions of the pores and eventual spreading of Pd on the pore walls. With the supports with relatively lower pore volume and surface area, Pd remains confined mostly to the external surface of the support and consequently in a less dispersed state. However, one cannot rule out some minor effects stemming from the make of alumina on the dispersion and deposition of Pd.

4.3. METAL–SUPPORT INTERACTION

In addition to the effect of surface area and pore structure of the supports on the dispersion of Pd, other more subtle factors like metal–support interaction need to be discussed. The BE data indicate an electronic interaction between Pd and alumina, and this interaction plays an important role in Pd dispersion. From the correlation between BE and dispersion of Pd, as depicted in fig. 4, it is observed that the dispersion decreases linearly as a function of BE ($Pd_{3d_{5/2}}$). Since a decrease in BE of Pd is indicative of partial electron transfer from the support to Pd, it is concluded that the extent of Pd dispersion is at least partly dependent on the extent of electron transfer from the support to Pd.

The above conclusion gains further support from the data displayed in fig. 5 which shows a systematic increase in Pd dispersion as a function of FWHM of the $Pd_{3d_{5/2}}$ peak. ESCA peak broadening [9–12] stems from (i) differential charging due to the insulating properties of the support, (ii) the presence of different oxidation states of the element and (iii) electronic interaction (i.e., carrier–catalyst interaction) between the support and the supported element. In the present situation, line broadening due to differential charging is ruled out because of the application of the charge compensating electron floodgun. Line broadening effect due to the presence of variously charged Pd species is a possibility, however, this is not considered in the present analysis because we have neglected the tailing ends and chosen only the central part of the deconvoluted peaks (representing the predominant zero oxidation state of Pd) for studying the line broadening phenomenon. In spite of this, a systematic broadening is noticed, and this we attribute to carrier–catalyst interaction arising from partial electron transfer from the support to the supported phase.

From the above discussion, it is concluded that in the present catalyst system, there is a considerable amount of carrier–catalyst interaction – an interaction arising from partial electron transfer from the alumina support to the supported Pd. This interaction is a major contributor to the dispersion of Pd on the support. Based on ESCA studies, this type of phenomenon of electron transfer to reduced supported metal from the support has been reported in the literature [13–17].

Although implicit in the above discussion, the extent of electronic interaction prevalent in the present catalysts is explicitly demonstrated in fig. 6. It shows a systematic increase in line broadening with decreasing BE that is caused by electron transfer from the support to the supported Pd.

4.4. CATALYST ACTIVITY

Pd-based catalysts are suitable for the hydrogenation of aromatic nitro compounds to the corresponding anilines [18]. This reaction has been used as a probe to evaluate the activity of the catalysts in the present work. The results, as given in fig. 7, show good correlations between hydrogenation activity and Pd dispersion and Pd : Al ratio, as determined by quantitative ESCA: higher Pd dispersion is conducive to higher activity, and accordingly, as the correlation between activity and Pd : Al ratio shows, more edge coated catalysts are less active.

5. Conclusions

The following conclusions are made from the present work:

(1) Useful information on the deposition and dispersion of Pd, supported on micron-size alumina powder supports, can be obtained by combined ESCA and carbon monoxide adsorption techniques.

(2) The dispersion of Pd on gamma alumina-supported catalysts, prepared by slurry-phase adsorption techniques, is dependent on several factors including the pore structure (pore volume and surface area) and the source of the alumina.

(3) The hydrogenation activity of the catalysts studied in this work is dependent on the percent Pd exposed, and consequently inversely proportional to the extent of metal aggregation at the pore mouths.

(4) The dispersion of Pd is correlated with carrier–catalyst interaction arising from partial electron transfer from the support to Pd.

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