

X-Ray Photoelectron Spectroscopy Studies of the Rhodium on Charcoal Catalyst

II. Dispersion as a Function of Reduction

J. S. BRINEN, J. L. SCHMITT, W. R. DOUGHMAN,
P. J. ACHORN AND L. A. SIEGEL

*Chemical Research Division, American Cyanamid Company,
Stamford, Connecticut 06904*

AND

W. N. DELGASS

*School of Chemical Engineering, Purdue University,
West Lafayette, Indiana 47907*

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A combination of X-ray photoelectron spectroscopy (ESCA) and X-ray diffraction measurements has been used to demonstrate the sensitivity of the dispersion of rhodium on charcoal catalysts to reductive environments at temperatures between 75 and 700°C. The measurements demonstrate that H₂ chemisorption is unreliable for the determination of rhodium dispersion for this catalyst system.

INTRODUCTION

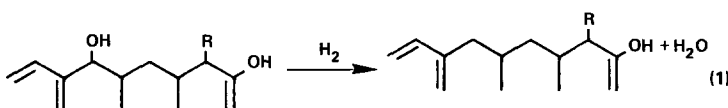
In a previous publication (1), Brinen and Melera examined the spectra of several rhodium on charcoal catalysts by X-ray photoelectron spectroscopy (ESCA). Attention was focused primarily on the different chemical species present on the catalyst surface and a correlation was established relating catalyst activity with the intensity ratio of oxidized rhodium to metallic rhodium observed by ESCA.

Conventional hydrogen chemisorption measurements (2) performed on these catalysts implied that the dispersion of rhodium on charcoal was independent of metal loading! To investigate this surprising result, a careful study of this catalyst was instituted to see whether ESCA

could be applied to monitor the physical properties of rhodium supported on charcoal, and to correlate the results with X-ray diffraction (XRD) and catalytic activity measurements.

EXPERIMENTAL METHODS

Rh/C catalysts were prepared by reduction of a solution of RhCl₃ containing commercially available activated charcoal (surface area of ~850 m²/g and pore volume of ~1.0 cc/g by N₂ BET method). The catalysts studied were nominally 12% metal although lower metal loadings were also employed for the chemisorption measurements. Relative catalytic activities were determined in a Parr hydrogenator [see, e.g., Ref. (3)] for the standard test hydrogenation reaction



For conventional dispersion determinations a dynamic flow hydrogen chemisorption technique was used (2). Nitrogen containing about 1% hydrogen was flowed continuously over the sample. Hydrogen adsorption peaks were recorded when a sample was cooled from 400°C to room temperature. By comparison with peak areas for known volumes of hydrogen, the hydrogen chemisorption was calculated. Heating and cooling cycles were repeated on each sample until the adsorption became constant.

ESCA spectra were measured on a Hewlett Packard 5950A spectrometer using monochromatic Al $K\alpha$ radiation. The spectrometer was equipped with a variable temperature probe and a flood gun used to neutralize the effects due to sample charging. The catalyst samples were examined either as smears on the gold plated sample mounts or were mounted on double sided sticky tape. The flood gun affected the binding energy measurements for the samples on the insulating sticky tape but had no effect on the spectra of samples smeared directly on the gold. For *in situ* reductions, H_2 was introduced into the spectrometer reaction chamber by means of a Varian 951-5100 leak valve. Pressures of up to 1 atm were used. When heating of catalysts was performed outside of the ESCA spectrometer, a tube furnace was used with an atmosphere of flowing H_2 or in some instances He.

The X-ray diffraction patterns were obtained by means of diffractometer scans. A conventional Philips unit was used with nickel filtered Cu K radiation at a scan rate of $0.5^\circ 2\theta/\text{min}$.

Crystallite sizes were estimated from the half width of the first rhodium line, using the customary formula

$$L = \frac{K \lambda}{B \cos \theta},$$

where the constant K is taken as 0.9, B is the half width and L the crystallite size.

No corrections were made for instrumental broadening.

RESULTS AND DISCUSSION

The rhodium dispersion, defined as (No. surface Rh atoms)/(total No. Rh atoms), was calculated from the chemisorption experiments assuming that one surface Rh atom chemisorbs one H atom (4). Results are shown in Table 1. The insensitivity of dispersion with respect to metal loading was unexpected and pointed to the possibility that physical changes were taking place on the catalyst surface during the chemisorption experiment. [For example, sintering of Pd/C catalysts under mild conditions has been reported (5).]

To pursue this point, a series of catalysts containing ~12% Rh were prepared and were subjected to various treatments prior to spectroscopic and chemical study.

A spectrum of the rhodium $3d$ lines obtained from a typical fresh catalyst is shown in Fig. 1, together with a similar spectrum of Rh_2O_3 . Note the presence of a substantial amount of oxidized Rh on the catalyst surface. The binding energy of the Rh $3d_{5/2}$ line for Rh_2O_3 is 308.0 eV which agrees with the surface oxide peak observed on the catalyst (1). The X-ray diffraction pattern of this catalyst shows no discernible pattern attributable to any rhodium species, implying that the rhodium present is either very finely dispersed or amorphous.

The solid curve in Fig. 2 shows a 50 eV wide scan containing both C $1s$ and Rh $3d$

TABLE 1
HYDROGEN CHEMISORPTION RESULTS

Catalyst	Loading ^a (%)	Rh dispersion ^b
A	3.3	0.10
B	6.5	0.12
C	11.9	0.12

^a Wt% Rh metal.

^b Defined as (No. surface Rh atoms)/(total No. Rh atoms).

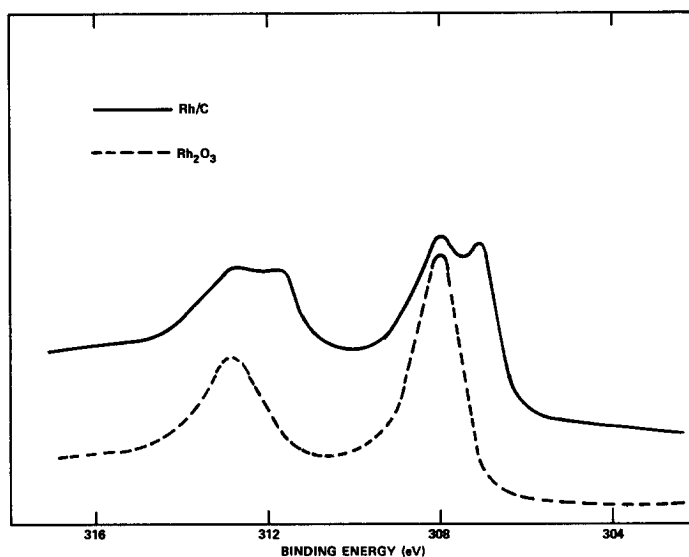


FIG. 1. A comparison of the spectra obtained for the Rh 3d lines from (—) fresh catalyst and (---) Rh₂O₃ demonstrating the presence of metal and oxide on the catalyst surface.

lines for the fresh catalyst while the broken curve shows a similar spectrum for the same catalyst heated in an atmosphere of hydrogen for 5 hr at 700°C before being transferred in air to the spectrometer. Note that the oxidized species has disappeared and that the Rh/C intensity ratio

has decreased as a result of the reduction. The Rh/C intensity ratio, determined from the areas under the C 1s line and the Rh 3d lines using 20 eV sweeps, can be used to monitor the relative amounts of surface rhodium accessible for ESCA detection and is related to the dispersion of rhodium

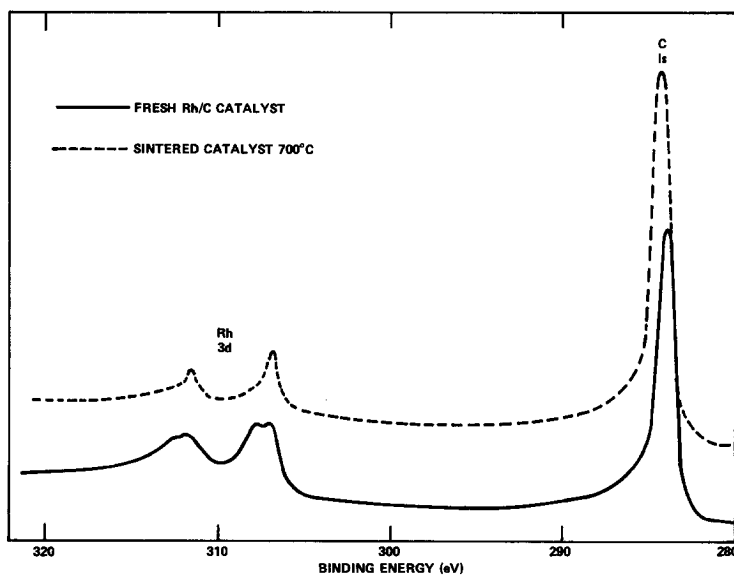


FIG. 2. Spectra obtained from (—) fresh and (---) sintered catalyst showing both the Rh 3d and C 1s support lines.

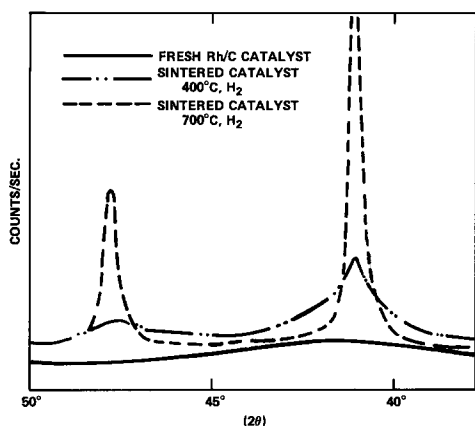


FIG. 3. X-Ray diffraction patterns for fresh and sintered catalysts.

on the charcoal surface. This experiment differs from Scharpen's (6) experiments, in which he varied the Pt loadings on the SiO₂ support. We are keeping the same rhodium loading and are monitoring its disposition as a function of treatment.

X-Ray diffraction patterns of the same catalysts described in Fig. 2 are shown in Fig. 3. The growth of large crystallites due to heating at 700°C in hydrogen is very apparent from the XRD patterns. Heating at lower temperatures and shorter times produces changes intermediate between those depicted in Figs. 2 and 3.

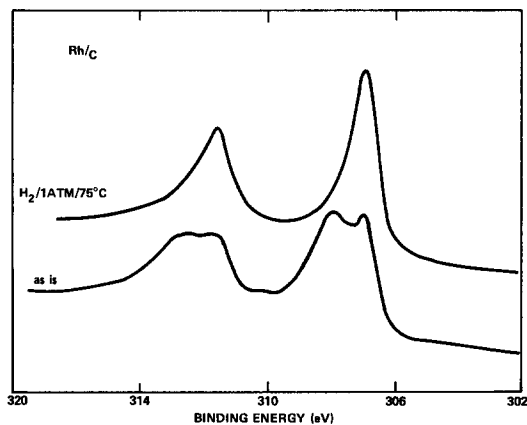


FIG. 4. Spectral changes in the Rh 3d lines as a result *in situ* H₂ reduction (in the spectrometer reaction chamber) at 75°C.

In order to minimize the possibility of unwanted reactions between the reduced catalyst and the environment during transfer, *in situ* reductions were performed in the spectrometer reaction chamber. The fresh catalyst was heated to 75°C in 1 atm of hydrogen for 30 min and the rhodium 3d spectra obtained before and after reaction are shown in Fig. 4. Note that the surface oxide species has disappeared even under these relatively mild conditions of reduction. In addition, the Rh/C intensity ratio is found to decrease upon reduction, both for *in situ* and external reductions. Concomitant with the decrease in Rh/C ratios (as the reductive conditions become more vigorous) is the formation of larger and larger crystallites as determined by XRD. A plot of ESCA vs XRD data is given in Fig. 5.

These results suggest that reduction in hydrogen at elevated temperatures affects the catalyst in at least two ways. The most obvious is that the surface oxide component on the surface undergoes reduction to the metal. As a result or in conjunction with this process the surface rhodium

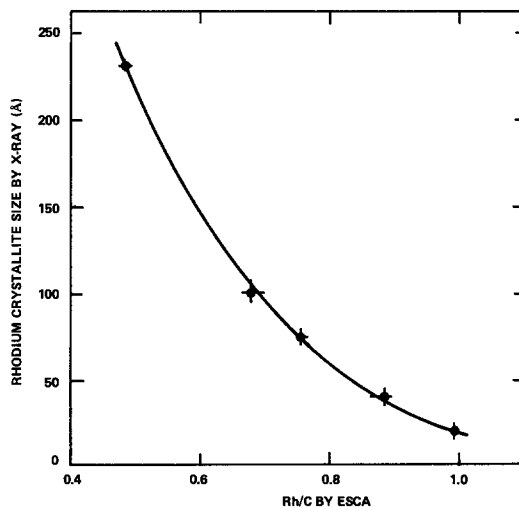


FIG. 5. A plot of the Rh/C intensity ratio vs Rh crystallite size determined from X-ray diffraction measurements.

atoms tend to "flow" resulting in the formation of larger clusters of metal. This is evident both from the decreased Rh/C intensity, which reflects changes in the rhodium distribution on the surface and from the X-ray diffraction results. Thus, the independence, with respect to metal loading of Rh dispersion measured by H₂ chemisorption, is due to sintering which occurred as a result of the chemisorption procedure. Indeed, the catalysts, after exposure to H₂ at 400°C, were sintered and contained large crystallites. Reoxidation of the sintered catalysts is not observed in the ESCA spectrum. This difference between sintered and fresh catalysts (which oxidize on exposure to air after the reduction step in the synthesis) suggests the difference in the oxidation/reduction behavior of Rh is a function of particle size. The sintered catalyst behaves more like a bulk metal which often shows an asymmetric photoelectron line due to adsorbed oxygen but not a well-split oxide line (7). The smaller particles present on the fresh catalyst, on the other hand, appear to be oxidized in bulk, giving a Rh₂O₃-like material.

The physical and chemical changes suggested by the spectroscopic results to occur on the surface of the catalyst should in turn affect the performance of the catalyst. To test this, the rate of disappearance of the reactant, R , and the first-order rate constant, K_w , were obtained as follows:

$$R = K_w \frac{K}{V} C,$$

$$K_w = \ln \frac{C_0}{C} \frac{1}{t} \frac{V}{W},$$

where R	moles of reactant reacted per hour
W	troy ounces Rh metal used
V	volume (liters) of reaction slurry
C_0	reactant concentration at $t = 0$ (moles/liter)
C	reactant concentration at time t (moles/liter)
t	reaction time (hours).

The results of this analysis together with the ESCA and XRD data are shown in Table 2. The percentage conversion and the first-order rate constant for the reaction decrease markedly as the dispersion decreases (as determined from the ESCA measurements) and the crystallite size increases (XRD).

CONCLUSIONS

ESCA and XRD measurements have been used to monitor changes produced by reduction at elevated temperatures in both the physical and chemical properties of a rhodium on charcoal catalyst. The measurements show that the conditions used in H₂ chemisorption measurements to determine dispersion are in themselves sufficient to damage the catalyst and degrade its performance. The results also reinforce

TABLE 2
SPECTROSCOPIC AND ACTIVITY RESULTS FOR STARTING AND REDUCED CATALYST^a

	(Rh/C) intensity	Crystallite size (Å)	% Relative conversion	K_w
Fresh catalyst	0.99	<40	100	16
H ₂ , 75°C, 30 min	0.82 (<i>in situ</i>)			
H ₂ , 400°C, 15 min	0.76	75	35	4
H ₂ , 700°C, 5 hr	0.47	235	<1	<0.1
He, 400°C, 15 min	0.85	40		
He, 700°C 2 hr	0.64	100		

^a ~12% Rh on charcoal.

the importance of ESCA intensity ratios as a measure of catalyst dispersion and suggest differences in the oxidation/reduction behavior of metals as a function of particle size.

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