XPS Study of the Reduction and Reoxidation of ZnO-Supported Palladium

During the past several years there has been a growing awareness that the support in a supported-metal catalyst can have a profound influence on both catalyst activity and selectivity (*1–5*). Several explanations have been offered as to the exact mechanism by which the support brings about such changes. In this note we will be concerned with metals supported on metal-oxide substrates. For this class of supports, the following has been suggested as one possible explanation of the observed influence of the support. During pretreatment or actual use, the supported metal facilitates a partial reduction of the support, with the degree of reduction depending on the metal oxide and the reduction conditions. The reduced-support species could then either donate electrons to the metal, accept electrons from the metal, or simply bond to the metal. Such interactions would change the electronic structure of the metal and could also affect the particle morphology. Evidence for an interaction between Rh and a reduced Zn species has recently been reported for a catalyst prepared by supporting $Rh_4(CO)_{12}$ on ZnO (*6*). In this note, we show that this type of metal–support interaction may be common for noble metals supported on ZnO. Specifically, we provide data which demonstrate that ZnO-supported Pd catalysts exhibit the same type of metal–support interaction that is observed for Rh/ZnO.

The Pd/ZnO catalysts were prepared from $Pd(NO_3)_2$ by using aqueous impregnation techniques. A 10% standard solution of $Pd(NO_3)_2$ was obtained from J. Bishop and Company. The ZnO (99.99%) was obtained from Alfa Products and had a surface area of ca. 7 m^2/g. Following impregnation, the catalysts were dried, and then calcined at 250°C for 3 hr. Catalysts with Pd loadings of 0.5, 1.0, 2.0, and 5.0% by weight were prepared.

X-Ray Photoelectron Spectroscopy (XPS) measurements were made with a PHI Model 550 ESCA/SAM spectrometer with a base pressure of 8×10^{-11} Torr. All data were obtained at room temperature with unmonochromatized $MgK\alpha$ radiation ($h\nu = 1253.6$ eV) and an analyzer resolution of 0.3 eV. The Zn $2p_{3/2}$ peak, which had previously been found to have a binding energy of 1021.8 eV, was used as an internal standard for determining binding energies (*6*). Reductions were conducted in a circulating atmosphere of H_2 (purity 99.9995%) within a sealed chamber attached to the ESCA/SAM spectrometer. The reduction conditions were 500 Torr H_2 at 250°C for 1 hr.

H_2 and CO chemisorption experiments as well as X-ray diffraction (XRD) studies were also attempted on several of the samples after various pretreatments. Unfortunately, because of the unique nature of these samples (see below) the chemisorption data were ambiguous. XRD powder patterns of the catalysts containing lower loadings of Pd did not exhibit peaks attributable to any Pd species. These data indicate that either the Pd in these catalysts is amorphous or of a particle size less than ca. 50 Å in diameter. From TEM studies on related catalysts in this laboratory, we estimate the Pd particle size in these catalysts at 30–40 Å in diameter.

Our XPS data for the four different loadings of Pd on ZnO were all very similar. For

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this reason, we will discuss only our data for the 2% loading. We should note that all of our experiments were repeated at least twice and the XPS binding energies were reproducible to ±0.1 eV. We should also note that no evidence for differential charging was observed on the reduced samples. Samples analyzed with and without a charge neutralizer were identical.

Our XPS data for 2% Pd supported on ZnO as a function of treatment are summarized in Figs. 1 and 2 and in Table 1. In the freshly calcined catalyst, the Pd $3d_{5/2}$ peak had a binding energy of 337.1 eV. This binding energy is consistent with Pd being present in the +2 oxidation state (7). Reduction in H_2 at 250°C caused the Pd $3d_{5/2}$ peak to shift to a lower binding energy (336.0 eV) (See Fig. 1 and Table 1). We note that this value is 1 eV higher in energy than that measured for the $3d_{5/2}$ peak in bulk Pd metal (335.0 eV). Exposing the reduced catalyst to air at 25°C for 30 min caused the Pd $3d_{5/2}$ peak to shift to an even lower binding energy (335.5 eV). Rereduction of the catalyst shifted the Pd $3d_{5/2}$ peak back to 336.0 eV (Fig. 1).

Turning our attention to the support, we find that reduction in H_2 also brought about a change in the Zn Auger spectrum (Fig. 2). Following reduction, a shoulder was present in the spectrum at a kinetic energy of 991.4 eV, close in energy to where Auger electrons from Zn metal are detected. The intensity of this shoulder indicates that a
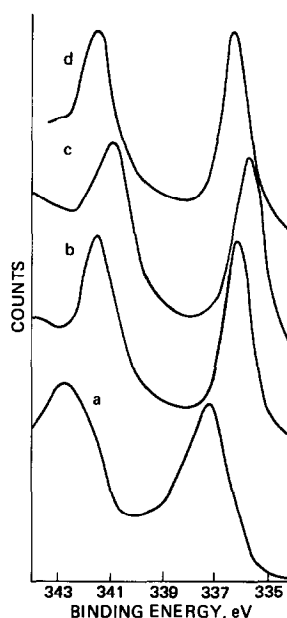

FIG. 1. Spectra of the Pd $3d$ peaks for a 2% Pd on ZnO catalyst as a function of pretreatment: (a) freshly prepared, (b) treated in H_2 at 250°C, (c) Sample b exposed to air at 25°C, and (d) sample c treated in H_2 at 250°C.

significant fraction of the ZnO surface has been reduced. This is contrary to previous experiments conducted with pure ZnO which demonstrated that ZnO is stable under these conditions (6). Indeed, little if any Zn metal should be produced under our reaction conditions based on thermodynamic arguments (6). The shoulder at 991.4 eV kinetic energy decreased markedly in intensity when the sample was exposed to air at 25°C (Fig. 2). From this we conclude that the reduced Zn species was easy to reoxidize. Rereduction of the sample again produced an intense shoulder at 991.4 eV (Fig. 2).

To explain the above observations, we conclude the H_2 treatment has induced a metal–support interaction. Specifically, we believe that during reduction the Pd facilitates a partial reduction of the ZnO. The Pd then interacts with the reduced Zn species giving rise to a surface containing Pd clusters on reduced Zn and possibly Pd–Zn bimetallic particles.
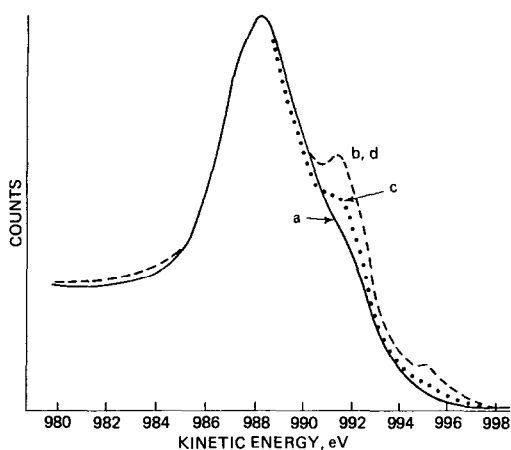
TABLE 1

ESCA Data for 2% Pd/ZnO

Treatment	Pd $3d_{5/2}$ binding energy[a] (eV)	Zn Auger kinetic energy[a] (eV)
None	337.1	988.4
H_2, 250°C (I)	336.0	988.2, 991.4
(I) followed by air, 25°C (II)	335.5	988.3, 991.3[b]
(II) followed by H_2, 250°C	336.0	988.2, 991.4

[a] Zn $2p_{3/2}$ peak at 1021.8 eV used as reference for binding-energy measurements. With this value for the Zn $2p_{3/2}$ peak, the Zn $3d$ was found to have a binding energy of 10.5 ± 0.05 eV.

[b] Peak at 991.3 eV is much reduced in intensity (see Fig. 2).

FIG. 2. Spectra of the Zn LMM Auger peak for a 2%
Pd on ZnO catalyst as a function of pretreatment: (a)
freshly prepared, (b) treated in H_2 at 250°C, (c) sample
b exposed to air at 25°C, and (d) sample c treated in H_2
at 250°C.

Such interactions would explain both the
apparent stability of the reduced Zn species
(6) and the high binding energy of the Pd
peak. From the literature, it is known that
the Pd $3d_{5/2}$ peak shifts to higher binding
energy when Pd is alloyed with other
metals (8). (Data for Pd–Zn alloys are un-
available.)

Exposure to oxygen, even at 25°C, dis-
rupts the interaction between the Pd and
Zn; i.e., this interaction is evident only in
an inert or reducing atmosphere. With the
disruption of the interaction, Zn would
reoxidize rapidly and the Pd would become
more like bulk Pd metal. This transforma-
tion would explain the shift of the Pd $3d_{5/2}$
peak toward a lower binding energy in an
oxidizing environment. The strong interac-
tion between Pd and Zn apparently changes
the normal chemisorption behavior of Pd.

This is in agreement with other systems
where metal–support interactions are ob-
served.

Finally, we note that both Pd/ZnO and
Rh/ZnO are good catalysts for methanol
synthesis from CO and H_2. In both of these
systems an interaction between the metal
and a reduced Zn species has been ob-
served following reduction in H_2. Although
it is difficult to prove that the Pd/Zn and Rh/
Zn species are the active sites in these cata-
lysts, they may play an important role in
the synthesis of methanol.

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