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Interaction of H_2 and CO with $Rh_4(CO)_{12}$ Supported on ZnO

INTRODUCTION

Ichikawa (*1*) recently reported that catalysts prepared by depositing Rh-carbonyl clusters on various metal-oxide carriers, e.g., ZnO, can be quite selective at converting CO and H_2 into oxygenated molecules. Furthermore, the distribution of products depended on the particular metal oxide. For example, when $Rh_4(CO)_{12}$ was supported on ZnO or MgO, methanol was produced selectively from CO and H_2, but when La_2O_3 was the support, the product contained mostly ethanol and methanol. Ichikawa ascribed these changes in selectivities to differences in the acid–base characteristics of the various supports. The situation may be more complex, however, in that metal-support interactions could be important. For example, rhodium could facilitate the partial reduction of some of the supports during H_2 pretreatment or during the actual catalytic reaction (*2*). We report here X-ray photoelectron spectroscopic (XPS) studies of $Rh_4(CO)_{12}$ supported on ZnO which show that heat treatments in H_2 cause just such a change in the ZnO.

EXPERIMENTAL

The Rh/ZnO catalyst was prepared as follows. $Rh_4(CO)_{12}$ (Strem) was dissolved in hexane and slurried with ZnO (Alfa Products, 7 m^2/g, purity 99.99%) under a dry nitrogen atmosphere. The hexane was then removed by vacuum evaporation. After the catalyst was dried no precautions were taken to avoid contact with air. The loading of rhodium on ZnO as determined by atomic absorption was 1.5 wt%.

Catalyst treatments consisted of heating the samples to 200°C, unless otherwise specified, for ~3 h in a static environment of gas (purity 99.99%) at 350 Torr in a preparation chamber attached to a photoelectron spectrometer. The XPS measurements were made on a PHI Model 550 ESCA/SAM spectrometer with a base pressure of about 8×10^{-11} Torr. Data were obtained at room temperature with unmonochromatized Mg $K\alpha$ radiation ($h\nu = 1253.6$ eV) and an analyzer resolution of 0.3 eV. Binding energies for selected support peaks were determined on the untreated materials by assigning the carbon 1*s* peak of the adventitious carbon to have a binding energy of 284.6 eV. Thereafter, these selected support peaks were used as internal standards.

RESULTS AND DISCUSSION

A. *ZnO Support* (*Untreated and Hydrogen-Treated*)

The Mg $K\alpha$-induced $L_3M_{4,5}M_{4,5}$ zinc Auger spectra for ZnO and metallic Zn are shown in Fig. 1. Table 1 lists the Auger kinetic energies and the binding energies of the $2p_{3/2}$ peaks. The Zn Auger peak was studied because shifts in its position and changes in its shape are sensitive indicators of the oxidation state of Zn. The Auger peaks for metallic Zn and ZnO differ by some 4 eV in kinetic energy.

To test the stability of ZnO toward reduction in H_2, we heated the oxide to 400°C in 350 Torr of H_2 for 2 h. After this treatment no change in shape or position of the Zn Auger peak was observed; the Auger spectra before and after treatment were identical. This finding is consistent with calculations of the free energy of formation for Zn metal and H_2O from ZnO and H_2; reaction is highly unfavorable for temperatures up to 750°C. Thus we conclude that ZnO is stable in H_2 at least to 400°C.

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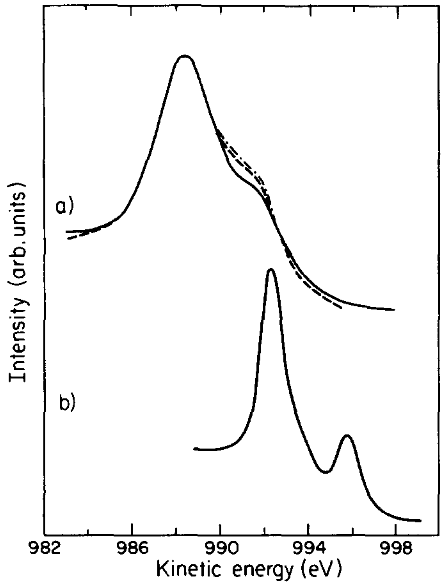

FIG. 1. (a) Solid line represents Zn $L_3M_{4,5}M_{4,5}$ Auger spectra for ZnO untreated as well as ZnO undergoing H_2 reduction up to 400°C. Also Zn $L_3M_{4,5}M_{4,5}$ Auger spectra for $Rh_4(CO)_{12}$ on ZnO after various heat treatments in hydrogen: —, untreated; ---, 200°C; —·—·, 400°C. (b) Zn $L_3M_{4,5}M_{4,5}$ Auger spectrum of Zn metal.

B. Rh Supported on ZnO—Untreated

Our data for the untreated catalyst are summarized in Table 1 and Fig. 2. The binding energy of the Rh $3d_{5/2}$ peak in this material is significantly greater than that of bulk Rh metal or Rh_2O_3 (*3*), and is close to that for unsupported $Rh_6(CO)_{16}$ (*4*). From the observed binding energy and other studies (*4, 5*), it appears that the Rh on this catalyst is highly dispersed, possibly still present as the intact carbonyl. As for the support, the addition of Rh to ZnO caused no changes in the Zn *LMM* Auger spectrum, indicating that in the freshly prepared catalyst the Rh and ZnO are unaffected by each other.

C. Rh Supported on ZnO—Heat Treated in H_2

Reducing the catalyst at temperatures up to 400°C in H_2 caused significant changes in both the supported Rh and the ZnO support. As the catalyst was heated to successively higher temperatures in H_2, the Rh $3d_{5/2}$ peak shifted to lower binding energy, to 307.1 ± 0.1 eV. The FWHM of the Rh $3d_{5/2}$ peak also decreased from 2.4 to 1.6 eV. The relative intensity of the Rh $3d_{5/2}$ peak as compared to that of the Zn $3d$ peak decreased as well with H_2 treatment (see Table 1). All of these observations are consistent with Rh becoming metallic and growing in particle size. If the H_2 treatment

TABLE 1

$Rh_4(CO)_{12}$ Supported on ZnO—XPS Data

Sample and treatment	Zn Auger kinetic energy (eV) $L_3M_{4,5}M_{4,5}$	Zn $2p_{3/2}$[a] (eV)	Rh $3d_{5/2}$[a] (eV)	$\frac{\text{Rh } 3d_{5/2}}{\text{Zn } 3d}$
ZnO				
Untreated	988.3	1021.8 (1.9)		
400°C + H_2	988.3	1021.8 (1.9)		
$Rh_4(CO)_{12}$/ZnO				
Untreated	988.4	1021.8 (1.9)	309.0 (2.4)	2.0
200°C + H_2	988.4 + Zn^0 shoulder	1021.8 (1.9)	307.2 (1.6)	1.9
400°C + H_2	988.5 + Zn^0 shoulder	1021.8 (1.9)	307.1 (1.6)	1.7
200°C + 2:1 H_2/CO	988.4	1021.8 (2.0)	309.0/307.8 (3.0)	1.6
Rh metal			307.0 (1.4)	
Zn metal	992.3	1021.5		

[a] Full width at half maximum is given in parentheses.

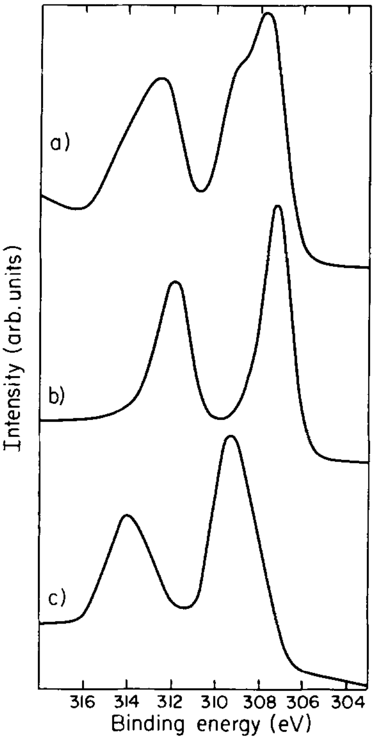

FIG. 2. Comparison of Rh $3d_{5/2}$ binding energies for $Rh_4(CO)_{12}$ on ZnO powder before and after heat treatments at 200°C for 3 h in various gases at several hundred Torr. (a) 2 : 1 H_2 + CO; (b) H_2; (c) untreated.

had simply reduced the Rh carbonyl compound with no appreciable sintering, a substantially higher binding energy for the Rh $3d_{5/2}$ peak should have been observed. Furthermore, the Rh $3d_{5/2}$/Zn $3d$ peak intensity ratio would not have been expected to decrease but rather remain constant or perhaps increase slightly. The data are summarized in Table 1 and Fig. 2.

Figure 1a shows spectra obtained from the Zn $L_3M_{4,5}M_{4,5}$ Auger peak for $Rh_4(CO)_{12}$ supported on ZnO powder as a function of sample treatment. The shape of the Auger peak changes progressively as reduction conditions are made more severe; *pure ZnO did not change under similar conditions*. The buildup of intensity at higher kinetic energy is indicative of Zn^{2+} that has been reduced to Zn^0. Such a reduction of ZnO was unexpected because of the stability of ZnO under our reaction conditions. Based upon the amounts of ZnO and H_2 involved and the equilibrium constant for the reaction $ZnO + H_2 \rightleftharpoons Zn + H_2O$ [calculated from available data, amount of catalyst used = 50 mg, reactor volume = 60 cm^3 (*6*)], $\sim 10^{-5}$ monolayer of Zn^0 should be formed under our static reaction conditions. From the Zn Auger spectra we calculate that ~0.4 monolayer of Zn^0 is present after reduction. To explain this apparent conflict, we conclude that the Rh somehow stabilizes the Zn^0, possibly as an alloy.

D. Treatment in H_2 and CO Simultaneously

Treating the catalyst in a mixture of 400 Torr of H_2 and 200 Torr of CO at 200°C for 3 h gave results quite different from those obtained with H_2. Only one Rh $3d_{5/2}$ peak was observed after H_2 treatment, but two were observed as a result of this treatment, at binding energies of 309.0 and 307.8 eV (Table 1, Fig. 2). Because the peak at 309.0 eV is similar to that of the untreated catalyst and because it is fairly intense, we believe much of the Rh must still be highly dispersed, possibly as Rh carbonyls, since the catalyst was cooled in the H_2/CO mixture. The presence of the second Rh $3d_{5/2}$ peak at 307.8 eV and the decrease in the Rh($3d$)/Zn($3d$) ratio also suggest that some sintering or agglomeration has occurred. Regarding the support, the shape of the Zn Auger peak did not change, i.e., the spectrum obtained after reaction was identical to that of the untreated material. These findings could mean that the interaction between Rh and CO is stronger than that between Rh and Zn and that Rh is no longer available to stabilize the Zn^0 species. More probably, however, the CO inhibits the absorption of hydrogen on the Rh, and insufficient hydrogen is present on the surface near the Rh to reduce the ZnO. Based on the above results, we have shown that even under mild reaction conditions metal-support interactions cannot be overlooked.

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