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NOTES

Copper Oxide Supported on Alumina

IV. Electron Spectroscopy for Chemical Analysis Studies

INTRODUCTION

Due to a lack of sufficiently sensitive electron detection systems, scientists in the early days of X-ray applications to spectroscopy elected to develop X-ray absorption edge spectroscopy rather than X-ray photoelectron spectroscopy. Siegbahn and co-workers (*1*) in Uppsala developed the first modern high-resolution X-ray photoelectron spectrometer and demonstrated its application to chemistry. They called their technique electron spectroscopy for chemical analysis (ESCA). We wish to report here an example of the application of ESCA to catalysis, namely, to the study of the dispersed surface phases of copper oxide supported on alumina.

In the Siegbahn technique, one irradiates a sample with an X-ray beam of a known constant frequency, and detects the intensity of a beam of electrons emitted from the sample as a function of their kinetic energy. After allowance for spectrometer corrections, the difference between the energy of the source, E_x, and the kinetic energy, E_k, equals the binding energy of the electrons in the atoms, E_b,

$$E_b = E_x - E_k - \Phi,$$

where Φ is the work function of the spectrometer.

On the other hand, in X-ray absorption edge spectroscopy, one monitors the intensity of the transmitted X-ray beam as a function of its frequency. In the X-ray photoelectron spectra, the electronic energy levels are observed as peaks, whereas in the X-ray absorption edge technique they show up as sharp discontinuities called edges. In both cases one can detect chemical shifts.

Previously, we have studied the copper oxide-supported-on-alumina system by XRD (*2*), EPR (*3*), and X-ray K-absorption edge spectroscopy (*4*). In addition, Selwood and co-workers (*5*) have studied this system using magnetic susceptibility measurements. The overall picture which emerged from these studies is that, depending on the ratio of the cupric ion concentration to the surface area of the alumina, the surface phase will assume the molecular structure of copper aluminate, $CuAl_2O_4$, or copper oxide, CuO, (*4*). With this background in mind, we have investigated the applicability of ESCA to the study of the structure of the supported catalysts, using the cupric system as a probe.

EXPERIMENTAL METHODS

The ESCA measurements were made on the Varian Associates Induced Electron Emission (IEE) prototype spectrometer (*6*). This instrument uses Al$K\alpha$ radiation (1486.5 eV) and incorporates the retardation voltage device to increase the resolution. Instead of determining the work function of the spectrometer which might change from one sample to another, the measured voltage for each sample was calibrated with the carbon 1s line which has a binding energy of 284 eV. The samples were ground to a fine powder and mounted on a cylindrical metal rod.

The procedure used in catalyst preparation has been described previously (*2, 3*). ESCA measurements have been made on

TABLE 1
BINDING ENERGY SHIFTS

No.	Sample: Cu (wt %)	Sample: Support surface area (m^2/g)	Sample: Calcination temp (°C)	Binding energy of $Cu2p_{3/2}$ (eV)	Shift of binding energy from Cu^0 value[a] (eV)	Shift of K-absorption edge from Cu^0 value[b] (eV)
I	$CuAl_2O_4$			934.20	3.20	7.94
II	CuO			933.25	2.25[c]	3.86[d]
III	10.3	72	500	933.35	2.35	4.50
IV	10.3	72	900	934.10	3.10	7.73
V	8.8	301	500	934.40	3.30	7.73

[a] Cu^0 $2p_{3/2}$ binding energy equals 931 eV; Ref. (*1*), App. 1.

[b] From Ref. (*4*).

[c] Compare with 2.5 ± 0.8 in Ref. (*7*).

[d] Compare with recently published value of 3.87 [Verma, L. P., and Agarwal, B. K., *J. Phys. C* 1, 1658 (1968)].

samples consisting of 8.8 wt % copper on Kaiser Chemicals, XA-331, γ-alumina with surface area of 301 m^2/g calcined at 500°C [run 5 in Table 1 of Ref. (*4*)] and 10.3 wt % copper on Harshaw 0104 γ-alumina with surface area of 72 m^2/g calcined at 500 and 900°C (runs 11 and 14, respectively). The reference materials, CuO and $CuAl_2O_4$, were the same used in the earlier X-ray K-absorption edge study (*4*).

RESULTS

Table 1 displays a summary of the binding energies of the $Cu2p_{3/2}$ L_{III} line for both reference and supported catalyst samples. For comparison in the last column we have included the X-ray K-absorption edge shifts with respect to copper metal. The accuracy of the binding energies is ±0.5 eV; however, the uncertainty in the relative shifts is of the order of only ±0.2 eV. Our result on the CuO is in good agreement with that reported in the literature (*7*). Figure 1 presents the actual form of the peaks. They all were recorded under the same conditions which demonstrates that the peak height is proportional to the percentage of Cu in the sample. The peak position was determined as the center of the horizontal line at half of the maximum peak height.

We have looked at the $Cu2p_{1/2}$ line for the CuO and $CuAl_2O_4$ and found the same shift, the binding energies were 968.0 and 967.5 eV, respectively. The Al2p spin doublet was not resolved and was the same for the aluminas and copper aluminate: 73.6 eV. The O1s line of $CuAl_2O_4$ and the aluminas were 530.7 eV and that for the

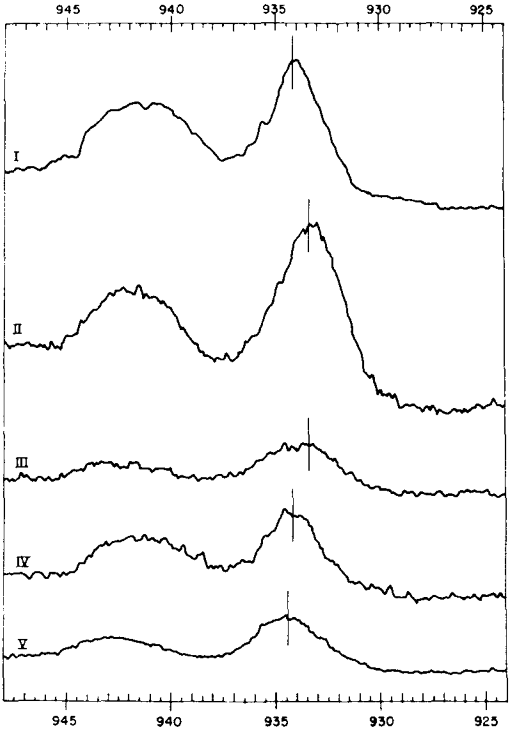

FIG. 1. ESCA spectra of supported copper and reference samples; sample numbering is the same as in Table 1.

CuO had a larger line width and was centered around 530.3 eV. Once more, although in all the quoted binding energies the absolute uncertainty was ±0.5 eV, the differences between samples did not exceed ±0.2 eV.

DISCUSSION

The current study demonstrates the feasibility of using ESCA to characterize the molecular structure of supported surface phases. Our results here support the earlier assignment of the surface phases. The high surface area alumina, 300 m^2/g, impregnated with about 10 wt % cupric ions and calcined at 500°C, assumes the copper aluminate structure; whereas the lower surface area alumina, 75 m^2/g, under the same conditions, forms copper oxide surface phase. Only upon calcination at 900°C does the copper oxide phase react with the support to form a copper aluminate phase. It is interesting to note that ESCA can differentiate between the binding energies of inner electronic shells of two cupric species, in which the only difference is in the oxygen packing around them and not in the valence state. Actually, one would expect splitting of the copper aluminate peak, as here we have a case of mixed spinel with copper ions distributed between octahedral and tetrahedral interstices (*8*). We could not detect this splitting. The difference in shifts observed in this experiment and the X-ray *K*-absorption edge measurements are due to the fact that we look at different quantities. Here we observe the binding energy of the $2p_{3/2}$ level, whereas, in the X-ray *K*-absorption edge measurement, one looks at the difference in energies between the 1*s* and the valence shell. ESCA can be used to look at the valence shell also. However, here one runs into several additional problems. The lines are broader, their intensities lower, and there are more chances of overlapping peaks from the different elements in the sample. In the future we believe that this range should be studied more carefully and then a more meaningful quantitative comparison between ESCA and X-ray *K*-absorption edge spectroscopy could be made. As far as our qualitative study goes, the results from the two techniques are in good agreement.

Our observations of the Al and O lines show that both have the same immediate environment in the alumina and the copper aluminate samples. Any perturbations of these lines due to the copper present in the aluminate are less than ±0.5 eV. On the other hand, the oxygen environment in CuO is quite different. Oxygen atoms are bonded only to copper atoms and in a distorted octahedral configuration. The broad peaks at about 8 eV higher binding energies observed for all the $Cu2p_{3/2}$ lines were observed for the $Cu2p_{1/2}$ lines too, but were not recorded in the Al2*p* and O1*s* cases. These peaks of lower kinetic energy possibly have their origins in transitions involving excited atoms or in secondary collisions between ejected photoelectrons and other atoms.

The advantages which we can foresee for ESCA over the other techniques which were applied to the copper-on-alumina case are the following. EPR (*3*) and magnetic susceptibility (*5*) studies are applicable to paramagnetic samples only. XRD (*2*) failed in many cases to detect surface phases below 10 wt % of supported material, and is completely ineffective in all cases below ~3 wt %. X-ray absorption edge (*4*) is limited to certain ranges in the periodic table and in many cases the resolution between the different cases is very low (*9*). It seems that ESCA does not suffer from all of these disadvantages, and has a great additional advantage of being able, in the same run, to look at all the other elements, except H and He, in the sample. The largest disadvantage of the technique would appear to be in the necessity for operation under high vacuum conditions.

CONCLUSION

ESCA promises to be a useful tool for the study of supported catalysts as well as pure chemical compounds which happen to be used as catalysts (*10*). It should be particularly valuable in establishing the structure of highly dispersed phases which cannot be characterized by XRD or other generally applicable techniques.

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Deuteriumolysis of Benzophenone

Catalytic hydrogenolysis of ketones and alcohols at a benzylic position to yield hydrocarbons with unchanged carbon skeleton is well established as a useful technique in organic synthesis (*1, 2*). Hydrogenolysis of ketones related to acetophenone and benzophenone and their derivatives has been used to obtain pure hydrocarbons for the American Petroleum Institute (*3, 4*). Deuteriumolysis of ketones is in principle an elegant and economical means for introducing deuterium at the benzylic position. A possible limitation (depending upon catalyst and conditions) is the exchange of aromatic protium by deuterium (*5–9*). We report that the deuteriumolysis of benzophenone (**Ia**) to diphenylmethane-α,α-d_2 (**IIa**) may be accomplished without detectable exchange of aromatic protium.

EXPERIMENTAL METHODS

*Reduction of Benzophenone (**Ia**)*

(a) Deuteriumolysis to diphenylmethane-α,α-d_2 (IIa). To a dry 300-ml hydrogenation flask containing 10 ml of CH_3CO_2D and 1.82 g of 10% Pd–C catalyst, prereduced with 60 ml of D_2, was added 9.1 g (0.05 mole) of **Ia** dissolved in 50 ml of CH_3CO_2D. Reduction at 25° at atmospheric pressure for 5.4 hr consumed 2535 ml of D_2. The catalyst was filtered out with Dicalite and the filtrate was made basic with 10% NaOH. Extracting with ether (2 × 200 ml), drying ($MgSO_4$), concentrating by rotary evaporation under reduced pressure, dissolving in 100 ml petroleum ether, bp 60–68°, and filtering through a 0.5-in. (o.d.) combination column (2 in. of silica gel on top and 1 in. of