

Surface Chemical-State Analysis of Metal Oxide Catalysts

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Key Words

K-Alpha, Catalysis, Copper Oxidation, Metal Oxides, Surface Analysis, XPS

The Thermo Scientific K-Alpha system was used to investigate the surface chemical composition of two catalyst samples. The first sample came from a batch that had shown the expected performance, but the second sample came from a batch that exhibited poor performance. Identification and quantification of the differences between the two samples was made using X-ray photoelectron spectroscopy (XPS), in an effort to understand the performance differences.

Introduction

Heterogeneous catalysts typically comprise of an active material dispersed upon a support. The active component is often a dispersion of transition metal particles, which may be in a completely or partially reduced form. The support material is commonly a metal oxide, such as alumina, and may also have a role in the catalytic process, either directly or by influencing the active material. Catalysts may be supplied in a precursor form, which needs activating prior to usage. As an industrial process relies on fixed operating conditions, any deviation from the correct precursor will result in failure of the process.

X-ray photoelectron spectroscopy is a widely used technique for catalyst analysis, delivering both elemental and chemical state information. Although the lateral resolution of XPS is greater than 10 μm it has the benefit of being a very surface selective technique; the data collected is representative of the outer 10 nm of the sample. This means that although individual particles cannot be measured, the average chemistry of the critical surface area of the catalyst can be determined and contrasted with that obtained from more bulk-sensitive methods.

In this study, two catalyst samples were analyzed. They had been obtained from a batch that had performed well in a process, and a batch that had performed poorly. The K-Alpha XPS system was used to measure both the elemental composition of the material and the chemical state of the components detected.



Method

The samples were supplied in coarse powder form. They were mounted as received onto the standard 60 \times 60 mm K-Alpha sample plate by pressing onto conductive carbon tape. The samples were then loaded into the K-Alpha fast entry airlock (FEAL), and pumped down. When the vacuum level in the FEAL meets the required level, the K-Alpha automatically transfers the samples into the analysis chamber. Typically, this occurs in less than ten minutes if the samples do not outgas significantly.

Each sample was analyzed to first determine the elemental composition and then chemical state of the chemical state of the elements detected. The elemental composition is found using a 'survey' scan, which encompasses the entire accessible energy range, and allows identification and quantification of the elements present at the surface. Based on the results from the survey scan, high resolution scans were collected and used to quantify the chemistry of the surface (please see Application Note 52297 for a full description of the acquisition process).

Results

Both samples had similar elemental compositions, as shown in Table 1, with the main differences being changes in the carbon and oxygen concentrations. This could be significant, but at these levels it is more likely to be due to small changes in surface contamination.

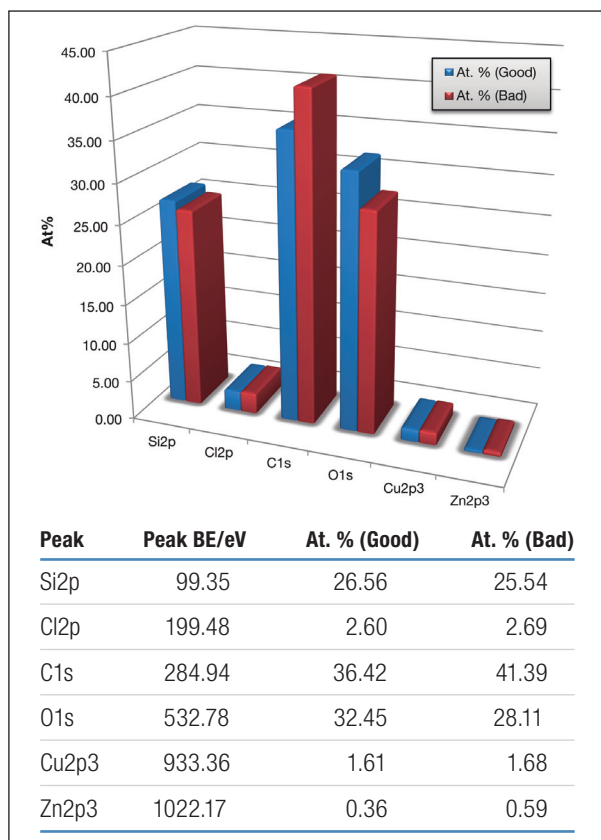


Table 1: Elemental composition of the “good” and “bad” samples based upon analysis of the survey spectra

Based on the elemental components found, high resolution scans were collected, and the Cu2p spectra for the “good” and “bad” samples are shown in Figure 1. The copper is completely oxidized, but there is a clear difference in the structure of the spectrum, which indicates that the mix of oxidation states present is different. In the “good” sample, the ratio of Cu(I):Cu(II) was 3:2; however, in the “bad” sample the ratio of Cu(I):Cu(II) is 1:3.

This variation in the surface oxidation state of copper could account for the differing performance of the two batches. These types of catalyst are typically reduced before use, and the standard reduction protocol may have resulted in non-optimal surface conditions for the “bad” batch.

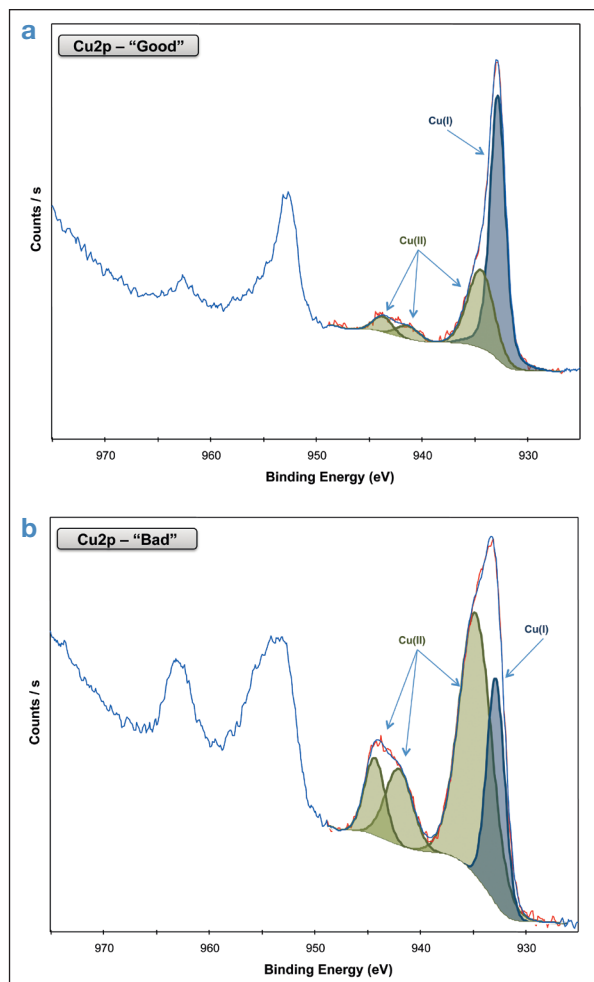


Figure 1: Cu2p spectra for (a) the “good” sample, and (b) the “bad” sample

Summary

XPS can be a valuable technique for the analysis of catalyst materials. Both conductive and insulating components can be analyzed with no special sample preparation, allowing all components of the catalyst to be investigated.

By using XPS, chemical differences between the surfaces of “good” and “bad” catalyst powders could be identified. The oxidation state of copper at the surface of the “bad” sample was higher than that of the “good” sample, evidenced in particular by the Cu2p XPS spectrum, which showed that more Cu(II) was present in the “bad” sample. This difference in the level of oxidation accounted for the variation in performance seen by the two batches.

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