JOURNAL OF CATALYSIS 34, 356–359 (1974)

Auger Electron Spectroscopic Study of the Surface Poisoning of Copper Catalysts

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Received December 4, 1973; revised April 18, 1974

Two samples of commercial copper catalysts were examined by Auger electron spectroscopy in search of an explanation for the difference in their performance as characterized by their ability to catalyze the reaction of methyl chloride with silicon metal. The poorly performing copper catalyst (Lot "B") was found to have at least three times the surface lead concentration that the good copper catalyst (Lot "A") did. The actual lead analysis (using the 92 eV NOO transition) on the surface of Lot B was 4.9 surface atomic percent as against 1.7% for Lot A. This low-energy transition has been shown to be more sensitive to surface analysis than the high-energy, 2275 eV, MNN transition. In relation to copper only, the lead level is about 13% in Lot B. These analyses represent analysis of the top few (1–2) layers of atoms. Such a high level of lead in Lot B catalyst is sufficient to substantially reduce or completely kill the catalytic activity. Examination of these catalysts by conventional physical and chemical analysis, scanning electron microscope and chemical analysis by EDAX, had failed to reveal any significant differences. Apparently, lead is migrating to the catalyst surface during a catalyst manufacturing step or steps and thus concentrating on the catalyst surface.

Introduction

Two copper catalysts of widely differing catalytic activity were analyzed by Auger spectroscopy to explain the difference in their performance. Such copper catalysts are used to catalyze the reaction of methyl chloride with silicon to produce methyl chlorosilanes (*1*). Conventional chemical analysis failed to show any significant differences (see Table 1). Known poisons for such copper catalysts are Pb, Sb, As and Bi (possibly Sn also) (*2*). However, Lot A catalyst (good) had 0.26% Pb as against 0.20% in Lot B catalyst (poor). Lead in much smaller amounts (~0.01%) can poison these catalysts (*2*). Chemical analysis of other elements and physical properties of the two catalysts appear to be the same (Table 1). Analysis by scanning electron microscope and by X-ray analysis (EDAX) also failed to show any meaningful differences. Since Auger electron spectroscopy (AES) is a highly sensitive tool for analyzing the top 2–10 surface atomic layers (*3–5*), such an analysis was performed on the two copper catalysts. This paper describes the AES analysis of the top few layers of the two lots of copper cat-

TABLE 1
Conventional Chemical Analysis of Two Commercial Copper Catalysts

	Lot A	Lot B
Copper metal	14.6%	18.8%
Cu_2O	48.2	56.2
CuO	31.1	22.0
Fe	0.98	1.2
Mg	0.20	—
Pb	0.26	0.20
Soluble SO_4	1.52	ND
Particle size	6.1 μm	5.5 μm
Surface area	0.5 m^2/g	0.65 m^2/g
Performance	Good	Poor

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alysts and shows how AES analysis of catalysts can be of tremendous help in identifying catalyst poisons.

Experimental Methods

The powdered catalysts obtained were pressed into thin wafers (5 × 20 mm) by compressing them in a stainless steel die (normally used in infrared work) at ~20,000 psi. This die had been used previously to compress other catalysts and no significant impurities were observed in Auger analysis of those catalysts. The catalyst wafer samples were then mounted on the carousel sample holder capable of holding 12 samples.

Auger electron spectroscopy as a surface analytical tool has been described recently in several review articles (*3–5*).

The analyses were performed using Physical Electronics Industries Auger spectrometer (Model 40-100), which was equipped with a cylindrical mirror analyzer and a grazing as well as normal incidence electron guns. However, normal incidence gun was used in this work since no surface charging problems were encountered.

Auger spectra of the two copper catalysts are shown in Figs. 1 and 2. Peak-to-peak heights of the major (largest size) Auger peaks of each element are converted into surface atomic percentages by dividing by the individual sensitivity factors. Sensitivity factors were obtained by comparing peak-to-peak heights of various characteristic Auger peaks with that of oxygen peak at ~510 eV (*6*). Surface atomic percentages given in Table 2 represent the normalized analyses of the top 2–10 layers of the catalyst. These analyses are not absolute but are self-consistent and trends are believed to be significant. Actual sampling depth is not known and is very difficult to determine, but for like composition materials, it should be identical.

The Auger peaks of each of the elements found in the two catalysts have been labeled with the symbols of the elements near the negative peaks in the differential of the secondary electron energy distribution in Figs. 1 and 2. The main spectrum in each figure covers the energy range of 0–2000 eV. However, lead has a pair of weak high-energy peaks at ~2170 eV and 2275 eV (MNN Auger transition), besides the characteristic strong low-energy peak at 92 eV (NOO Auger transition). The high-

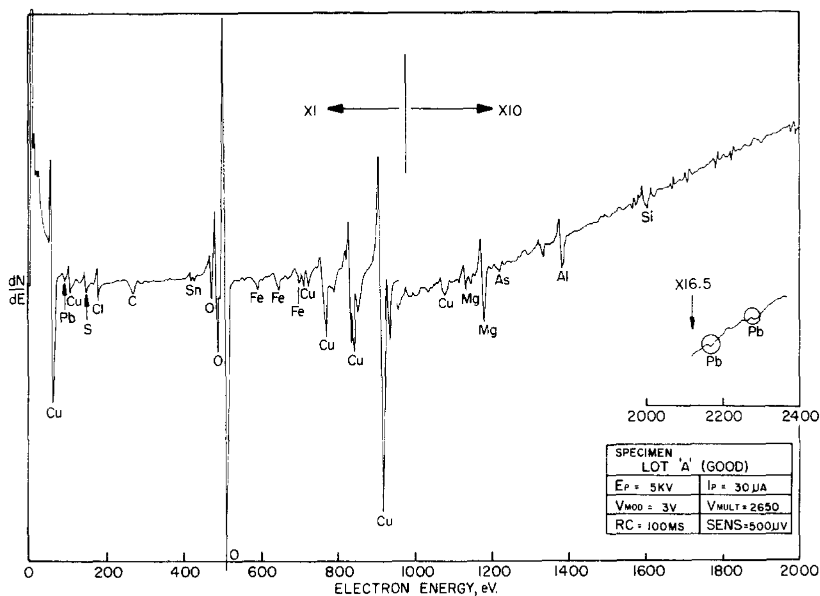

Fig. 1. Auger analysis of copper catalyst, Lot A (good).

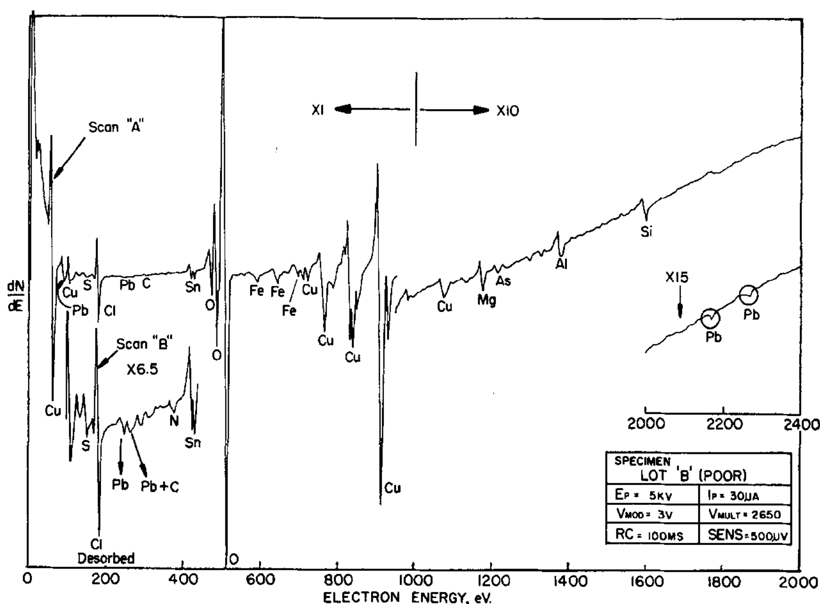

FIG. 2. Auger analysis of copper catalyst, Lot B (poor).

energy peaks are shown in the scan in the right corner in Figs. 1 and 2.

DISCUSSION

It is quite evident from Figs. 1 and 2 and Table 2 that Lot A has about one-third as much lead as Lot B based on the low-energy peak belonging to the NOO transition. However, the difference in Pb levels of the two samples is less pronounced when comparing the high-energy peaks of the MNN transition. This is to be expected when the impurity is concentrated toward the top surface atomic layer. The escape depth for the high-energy transition may be about tenfold deeper than that for the low energy NOO transition. The level of lead in Lot B is 4.9 surface atomic percent of all elements including oxygen. In relation to copper, however, the lead level is about 13%. It should be emphasized here that the Auger analysis given (using NOO transition) represents the analysis of the top few (1–2) layers of the surface (*6*). Thus, if lead is concentrated more towards the top surface atomic layer, the level of lead could be even higher. Furthermore, since all surface Cu atoms may not be catalytically active, 13 atoms of lead/100 atoms of Cu can very well explain the inactivity of Lot B catalyst.

The fact that catalyst, Lot B, has a higher concentration of lead on the copper surface despite having a lower total lead content could be explained in a variety of ways. Extended roasting of the catalyst during its manufacture is known to result in an inactive product. This would suggest

TABLE 2
AUGER SURFACE ELEMENTAL ANALYSIS OF COPPER CATALYSTS

Element	Sensitivity factor	Surface atomic (%) Lot A	Lot B
Sulfur	1.5	0.88	0.31
Chlorine	1.5	1.47	1.49
Lead	0.4	1.66	4.89
Carbon	0.3	ND	Tr
Tin	2.0	0.33	0.45
Oxygen	1.0	38.64	39.30
Iron	0.5	2.43	2.23
Copper	0.5	50.34	49.16
Magnesium	0.4	1.52	0.56
Arsenic	0.1	0.55	0.56
Aluminum	0.25	1.35	0.71
Silicon	0.20	0.83	0.33
Copper/lead ratio		23.3	8.04

that the lead may be concentrating on the catalyst surface as a result of its migration to the grain boundaries during the roasting step.

Some of the other significant differences in the two catalysts are summarized below:

1. Copper catalyst, Lot B, had much higher surface Cl, at start of Scan "A" of the Auger spectrum; however, some of the chlorine desorbed under the incident electron beam. This phenomenon is quite typical of some of the well-known chlorides.

2. The level of sulfur in Lot A was three times higher than in Lot B. This form and level (0.88%) of sulfur is obviously not deleterious to the function of the good catalyst; namely, Lot A. Bulk analysis indicates that it is present as sulfate.

3. The levels of tin, iron and arsenic are roughly the same in the two catalysts.

4. The levels of aluminum and magnesium are 2–3 times higher in the good, active catalyst (Lot A) than in the inactive catalyst. What role these impurities play in the performance of such copper catalysts is open to speculation, although they are known to be promoters for the copper catalyst (*1*).

5. No significant amounts (~0.1 atomic percent) of Bi or Sb, the other poisons, were detected in the two catalysts analyzed.

Conclusions

1. The surface level of lead in Lot B copper catalyst (poor) is three times the level detected in Lot A copper catalyst as observed by Auger electron spectroscopy of these catalysts. Lead is a known poison for such copper catalysts. Although the actual level of lead on the top atomic layer (i.e., the catalytic surface) was not estimated, the amount of lead found on Lot B catalyst (poor), in relation to copper, is sufficient to substantially reduce or completely kill the catalytic activity. Lead is apparently migrating to the surface during some step or steps in the catalyst manufacture.

2. The low-energy Auger transition of lead (NOO at 92 eV) is shown to be more sensitive to surface analysis than the high-energy Auger transition (MNN at 2170 and 2275 eV).

3. The results of this study illustrate the remarkable high sensitivity of Auger electron spectroscopy to surface, as opposed to bulk, composition, and the usefulness of such an analysis in the study of catalysts and catalytic behavior.

4. Typical analysis time per sample was less than 1 hr. Complete high sensitivity, elemental analysis for most of the periodic table, in such a short time has not heretofore been possible.

5. A better estimate of top surface atomic layer and subsurface layer composition can be obtained by running in-depth concentration profiles by well-known inert ion sputtering techniques.

Acknowledgment

The author acknowledges the assistance of Dr. P. W. Palmberg of Physical Electronics Industries. Scanning electron microscope and EDAX analyses were performed by Dr. W. C. vonDohlen and Mr. E. R. Walter. The author also expresses his appreciation to Union Carbide Corporation for approval to publish this work.

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