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Studies of the Methanation Catalysts $ThNi_5$ and $ZrNi_5$ by Auger and Characteristic Energy Loss Spectra*

A. G. MOLDOVAN, A. ELATTAR, AND W. E. WALLACE

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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$ThNi_5$ and $ZrNi_5$ (fresh, used, and H_2S poisoned) have been examined by Auger spectroscopy (AES) and Characteristic Energy Loss Spectroscopy (CELS) to elucidate the strikingly different behavior of these materials as methanation catalysts. With use $ZrNi_5$ is transformed into Ni supported on ZrO_2 and $ThNi_5$ into Ni supported on ThO_2. AES indicates that the Ni on ZrO_2 is heavily overlaid with graphite. This does not occur with Ni and ThO_2, accounting for the exceptional activity of this catalyst compared to Ni on ZrO_2. Plasmon excitation energy determined from CELS are consistent with this picture. The large amount of surface Ni for the transformed $ThNi_5$ catalyst accounts for its high resistance to H_2S poisoning compared to that of $ZrNi_5$. A strong CELS peak is observed at 6.5 eV in $ZrNi_5$ and $ThNi_5$ as well as in elemental Ni, suggesting a very similar band structure for these materials. In this respect Ni and the Ni intermetallics are similar to Co and Co intermetallics as deduced from photoemission studies and recent APW band calculations.

I. Introduction

Intermetallic compounds MNi_5, where M represents Th, U, or Zr, have recently been shown (*1, 2*) to be catalytically active in the formation of CH_4 from CO and H_2. During the course of the reaction the catalyst is observed to be extensively transformed. The surface area per gram increases by a factor of 20 or 30 and the X-ray diffraction pattern changes from one characteristic of the intermetallic to one produced by a mixture of Ni and MO_2.

$ThNi_5$ and $ZrNi_5$ are of particular interest. The former has a specific activity exceeding that of a conventional silica supported Ni catalyst by about an order of magnitude, whereas $ZrNi_5$ has specific activity comparable with that of Ni/SiO_2 (*1*). $ThNi_5$ exhibits exceptional resistance to poisoning by H_2S while $ZrNi_5$ is quite susceptible to deactivation by H_2S. It has been surmised that Ni in these (and in the closely related RNi_5 series (*3, 4*), where R is a rare earth) is the catalytically active species in each case. If so, the contrasting behavior of these two materials implies significant differences in the nature of Ni in the used catalysts. The present study was initiated in an effort to reveal and elucidate these differences by means of Auger spectroscopy (AES). In the course of the study the Characteristic Energy Loss Spectra (CELS) were also determined.

II. Experimental Technique

The intermetallic compounds were formed by fusing together stoichiometric proportions of the component metals of high purity (99.9% or better, disregarding nonmetallic impurities such as C, O, etc.). The fusion took place in a water-cooled copper boat under an at-

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mosphere of purified argon. Power was supplied by a 10-kW radiofrequency generator. Existence of the compound in the desired structure was confirmed by conventional X-ray powder diffraction results. Samples as prepared are very brittle. They were ground to a fine powder in air and a portion was examined by AES whereas another[1] was used in the reactor for 50 to 100 hr and then examined by AES. Samples were pressed into pellets ~0.5 cm. in diameter, placed in the bell jar of the spectrometer and evacuated to 10^{-10} Torr for two days prior to examination by AES.

High-resolution Auger spectra were recorded using a Varian Model 981-2730 spectrometer. Spectra were obtained with a primary beam of 2 keV and 1 μA/cm^2. A 100-kHz and 2v-peak-to-peak modulation was applied to the CMA. To establish the stability of the surface under the electron bombardment the peak-to-peak heights of carbon, oxygen, and sulfur were monitored at 15-min intervals for 3 hr. No significant changes were observed. The sputtering was carried out using an Ar$^+$ beam. The ion beam current was 1 μA at 3 keV. The AES spectra were recorded immediately after sputtering.

CELS were obtained at primary beam energies (E_p) of 250, 500, and 1000 eV.

III. Results

A. Auger Spectra[2]

The ZrNi$_5$ fresh catalysts showed no significant surface segregation. From the peak-to-peak heights of the Zr and Ni lines it was established, using the method developed by Hall *et al.* (5) that the stoichiometry of the surface is ZrNi$_x$ with $x = 5 \pm 1$. The surface is covered with an oxide layer whose thickness is estimated to be half the escape depth of the electron generated by the Ni–$L_3M_{4,5}M_{4,5}$ transition. This estimate was obtained by comparing the intensity ratios of this transition for ZrNi$_5$ and for elemental Ni used as a standard, both intensities being normalized to the elastic peak. A pronounced carbon peak was observed in the Auger spectra for both ZrNi$_5$ and ThNi$_5$; this is ascribed to carbon impurity in the metals used to prepare the catalysts.

AES for used ZrNi$_5$ is shown in Fig. 1a. There is a large carbon signal indicative of

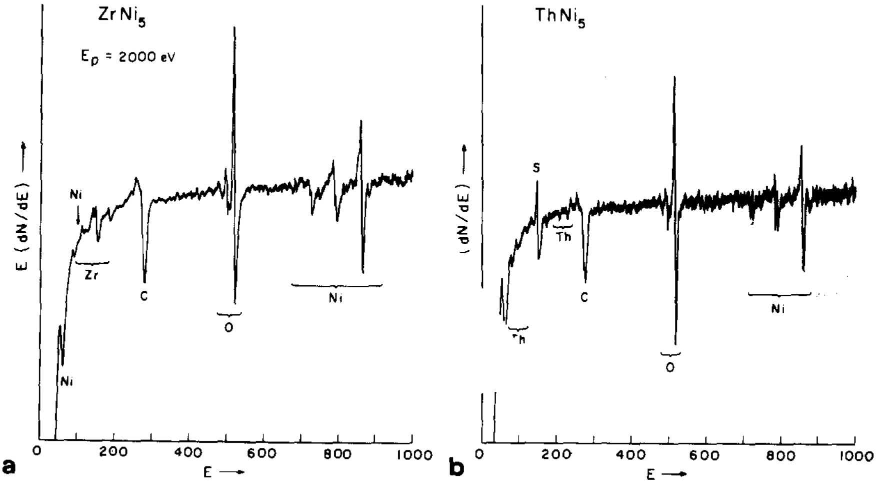

FIG. 1 (a) AES spectrum of ZrNi$_5$ used catalyst. (b) AES spectrum of ThNi$_5$ used catalyst.

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[1] These are termed “used” rather than “spent” catalysts since the material does not become “spent” with use. Instead, catalytic activity initially increases with time during the period of examination.

[2] In the interest of brevity only representative AES and CELS are shown.

TABLE I

PEAK-TO-PEAK HEIGHTS (IN MILLIMETERS) IN $ZrNi_5$ AND $ThNi_5$

	$ZrNi_5$			
	$Ni(L_3M_{4,5}M_{4,5})$	$C(KVV)$	$Zr(M_4N_{2,3}M_{4,5})$	$O(KVV)$
Fresh	82	56.5	20	148
Used	36.5	91	14.5	91.5
Ratio[a]	0.45	1.61	0.73	0.62

$ZrNi_5$–Relative intensities

$$\frac{C(\text{fresh})}{Ni(\text{fresh})}\Big/\frac{C(\text{used})}{Ni(\text{used})} = 0.28$$

$$\frac{C(\text{fresh})}{Zr(\text{fresh})}\Big/\frac{C(\text{used})}{Zr(\text{used})} = 0.45$$

$$\frac{C(\text{fresh})}{O(\text{fresh})}\Big/\frac{C(\text{used})}{O(\text{used})} = 0.38$$

	$ThNi_5$			
	$Ni(L_3M_{4,5}M_{4,5})$	$C(IVV)$	$Th(O_2O_{4,5}O_{4,5})$	$O(IVV)$
Fresh	21	52	5.5	117.5
Used	39	48.5	7	141.5
Ratio[a]	1.9	0.93	1.3	1.20
Poisoned	43	73.5	9.5	204
Ratio[a]	2.0	1.4	1.7	1.73

$ThNi_5$–Relative intensities

	Poisoned
$\frac{C(\text{fresh})}{Ni(\text{fresh})}\Big/\frac{C(\text{used})}{Ni(\text{used})} = 2.0$	1.42
$\frac{C(\text{fresh})}{Ni(\text{fresh})}\Big/\frac{C(\text{used})}{Th(\text{used})} = 1.39$	1.21
$\frac{C(\text{fresh})}{O(\text{fresh})}\Big/\frac{C(\text{used})}{O(\text{used})} = 1.29$	1.23

[a] Intensity of the signal coming from the used or poisoned compared to fresh material.

weakly bonded carbon. Peak-to-peak (p–p) heights for $Ni(L_3M_{4,5}M_{4,5})$, $C(KL_2L_2$ or $KVV)$, and $Zr(M_4N_{2,3}N_{4,5})$ in used $ZrNi_5$ compared to fresh $ZrNi_5$ are given in Table I, as well as the signal strengths of O, Ni, and Zr compared to that of carbon. It is noted that the intensities of Ni, Zr, and O peaks have decreased for the used catalyst whereas that of

C has increased. The decrease in the oxygen signal is not unexpected in view of the reducing atmosphere to which the catalyst had been exposed. The decrease in the Ni and Zr peaks is ascribed to chemisorbed carbon. The larger decrease of the Ni signal compared to Zr indicates that the chemisorbed carbon is on the Ni sites formed at the surface of the catalyst.

AES were obtained for fresh $ThNi_5$, used $ThNi_5$ and used $ThNi_5$ deactivated with H_2S. The relative intensities of the Th and Ni signals for fresh $ThNi_5$ suggest a surface slightly nickel enriched over the bulk stoichiometry. The fresh $ThNi_5$ and used $ThNi_5$ (Fig. 1b) showed a distinct sulfur signal which we regard as spurious. It probably originated with

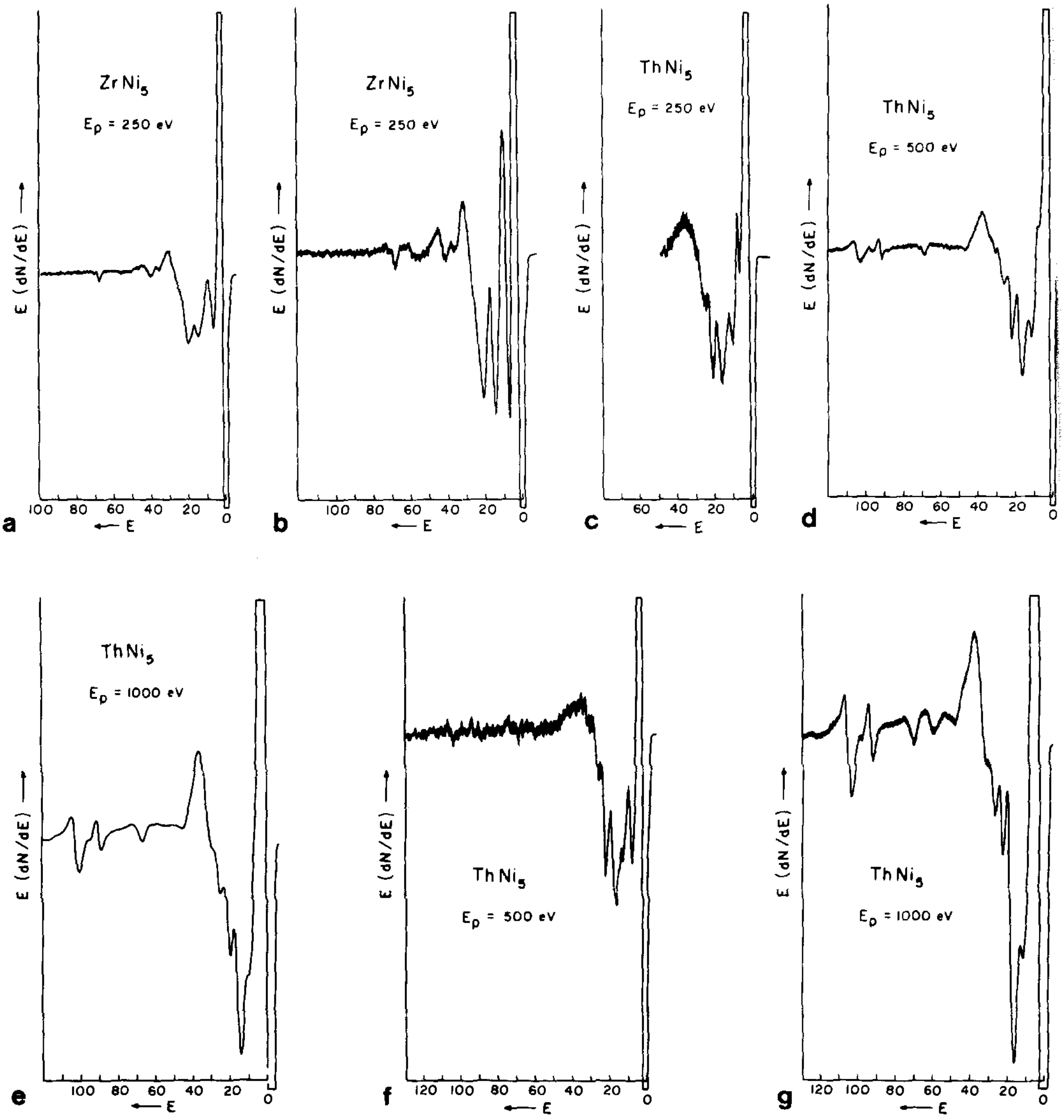

FIG. 2 (a) CEL spectrum of $ZrNi_5$ fresh catalyst. (b) CEL spectrum of $ZrNi_5$ used catalyst. (c) CEL spectrum of $ThNi_5$ fresh catalyst. (d) CEL spectrum of $ThNi_5$ fresh catalyst. (e) CEL spectrum of $ThNi_5$ fresh catalyst. (f) CEL spectrum of $ThNi_5$ used catalyst. (g) CEL spectrum of $ThNi_5$ used catalyst.

the sulfur-poisoned catalyst which had been placed in the bell jar along with the fresh and used $ThNi_5$. Strong O and C peaks were observed. Ion bombardment reduced the oxygen peak but the C p–p height remained practically unchanged, indicating a carbide.

Used $ThNi_5$ shows a Ni signal (Table I) increasing roughly twofold whereas the Th signal either increases only slightly or is not significantly changed. Thus in the used catalyst the surface has become significantly enriched in Ni. For the poisoned $ThNi_5$ the p–p height for the sulfur signal is increased by a factor of 3.1 over that for the used catalyst (Fig. 1b). The Ni signal is somewhat reduced (compared with the C signal) by H_2S poisoning but not as strongly as would be expected if it were merely overlaid by sulfur. Evidently the Ni is converted to Ni_3S_2 which is also indicated by the X-ray diffraction pattern of the poisoned catalyst. Unlike $ZrNi_5$ the oxygen signal for $ThNi_5$ increases for the used catalyst compared to the original material. The carbon signal is substantially the same for fresh and used $ThNi_5$, again in contrast with the behavior of $ZrNi_5$, but is increased by about 40% for the H_2S poisoned material. There is also a very substantial increase in the oxygen signal ($\sim$75%) for the H_2S poisoned material (Table I).

B. Characteristic Energy Loss Spectra

When an electron impinges upon a solid, it can lose energy in a variety of ways–it can excite electrons from one band to another (interband transitions), ionize the localized electrons in atoms, generate plasmons (i.e., excite the plasma oscillations in the sea of delocalized electrons), etc. These effects are revealed in peaks in plots of intensity versus energy on the low-energy side of the elastic or strong Auger peaks. Plasmon excitations involve typically energies of 10–50 eV.

CELS results for $ZrNi_5$ and $ThNi_5$, fresh

TABLE II

CHARACTERISTIC ENERGY LOSS SPECTRA[a]

	Ionization energies (eV)					
	O	O	Ni	Zr	Th	Th
	2*s*	2*p*	3*p*	4*s*	6*s*	5*d*
$ZrNi_5$(fresh)	24.5	n.o.[b]	67	n.o.	—	—
$ZrNi_5$(used)	n.o.	n.o.	69	52.0	—	—
$ThNi_5$(fresh)	24.5	10.5	68	—	n.o.	87.5
$ThNi_5$(used)	25.5	n.o.	68.5	—	58.5	88.5

	Plasmon Energies (eV)					
	Surface	Bulk intermetallic	Bulk oxide	2nd surface harmonics	2nd harmonic intermetallic	2nd harmonic bulk oxide
$ZrNi_5$(fresh)	14.0	19.5		35.0(?)[c]	40	
$ZrNi_5$(used)	14.0		22.0	36.0(?)		42
$ThNi_5$(fresh)	16.0		21.0	31.5(?)		
$ThNi_5$(used)	14.5		21.0	31.5(?)		43

[a] In addition, all four samples showed a very strong peak at 6.5 eV, which is ascribed to an interband transition. The instrumental energy resolution is $\sim$0.5 eV.

[b] Indicates not observed.

[c] These appear to be second harmonics but the exact assignment—whether surface or bulk, oxide, nickel, or intermetallic, is uncertain.

and used, are given in Figs. 2a to g and in Table II. Since the resolution of the spectrometer is proportional to the energy of the primary beam, the gross features of the CEL spectra show some variation with E_p. The ionization energy assignments can be made unambiguously; the plasmon energies are tentative. The ionizations are identified from the known energies (*6*) for the process. In identifying the plasmon peaks use is made of the relationship (*7*) $E_{\text{surf}} = E_{\text{bulk}}/(1 + \varepsilon)^{1/2}$ where ε is the dielectric constant. When $\varepsilon = 1$, the energies differ by $2^{1/2}$. This value for ε was assumed in our calculation. Use is also made of line shape, which is different for plasmon excitation than for ionization, correlation of intensity of the line with the chemical nature of the surface, as inferred from the AES, etc.

A very pronounced peak is observed at 6.5 eV in all four samples and in elemental nickel. This is ascribed to an interband transition.

IV. Discussion

The AES data for $ThNi_5$ show that the surface of the used catalyst is enriched in Ni compared to the starting material. For $ZrNi_5$ the opposite is true; the strength of the Ni signal for $ZrNi_5$ suggests a surface which is Ni-impoverished with respect to fresh $ZrNi_5$. These observations are consistent with the superior catalytic features of $ThNi_5$ if Ni is taken to be the catalytically active species. The AES carbon peak in $ZrNi_5$ (used) is characteristic of weakly bonded graphitic carbon; the corresponding peak in $ThNi_5$ (used) has a shape of carbide carbon. It is to be noted in Table I that with use the carbon signal in $ZrNi_5$ increases while the other signals—Ni, Zr, and O—decrease. The Ni signal decreases by over 50%. In contrast with this behavior the Ni, Th, and O signals for $ThNi_5$ increase in intensity while the carbon signal decreases slightly with use.

These observations are consistent with the following concept: With use $ZrNi_5$ decomposes into Ni and ZrO_2 (Ni/ZrO_2), but at the same time it becomes extensively overlaid with graphitic carbon so that much of the Ni is rendered catalytically inactive. For $ThNi_5$ there is no indication of the deposition of graphitic carbon. The carbon signal indicates carbide which was contained in the fresh material. There is no indication of a carbon buildup on the catalytically active Ni.

Thus the AES results provide a plausible experimental basis for the differing behavior of $ThNi_5$ and $ZrNi_5$. However, they leave unanswered the question as to why graphitization occurs in one case and not the other. These two intermetallics differ in structure. $ThNi_5$ and $ZrNi_5$ are hexagonal and cubic, respectively. The differing structure may lead to differing morphology in the decomposition products. This, or possibly the different character of Ni (segregated) on ThO_2 and ZrO_2, or a combination of the two, may produce the higher activity for Ni/ThO_2. Evidently Ni/ThO_2 is sufficiently active to convert adsorbed carbon complexes into hydrocarbons, which then vaporize away. Ni/ZrO_2 is less active and the adsorbate graphitizes.

The CELS results are not inconsistent with the observations based upon AES. In $ThNi_5$ (used) a plasmon excitation at 31.5 eV is observed, which is most likely ascribable to nickel in the Ni-rich surface. This excitation is not observed for $ZrNi_5$ (used), probably because the Ni is buried too far beneath the graphite.

The AES and X-ray diffraction results indicate that the $ThNi_5$ (used) is poisoned by H_2S by converting the active Ni to Ni_3S_2. The heightened susceptibility of $ZrNi_5$ (used) to H_2S poisoning is undoubtedly a consequence of the small amount of Ni exposed and hence active.

The fact that the interband transition occurs at 6.5 for both $ZrNi_5$ and $ThNi_5$ as well as for elemental Ni is of very considerable interest. Photoemission studies by Cuthill *et al.* (*8*) on $SmCo_5$ and $PrCo_5$, having structures closely related to $ZrNi_5$ and $ThNi_5$, showed a band structure for the materials very similar to elemental Co. APW band structure calculations by Arlinghaus (*9*) and by Malik *et al.* (*10*) for $SmCo_5$, YCo_5, and $GdCo_5$ confirm this similarity. The fact that the strong interband transition occurs at 6.5 eV for elemental Ni, $ZrNi_5$, and $ThNi_5$ implies a similar band structure for these three materials and in this respect the three nickel compounds closely resemble the behavior of Co and the several RCo_5 compounds.

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