

hydrogenation reaction. It is known that ThNi_5 decomposes to Ni/ThO_2 under reaction conditions (21). It was found by Elattar et al. (22) that preparation of Ni/ThO_2 by intermetallic compound decomposition gave a catalyst significantly more active for the methanation reaction than one prepared by the standard wet chemical techniques.

Elattar et al. investigated decomposed NdMn_2 , GdMn_2 and ThMn_2 for methanation activity, but found no production of methane (22). They tried ThFe_5 and CeFe_2 and found activity for methanation to begin at 200°C and peak at 450°C . At the latter temperature, 50 to 75% of the carbon monoxide had been converted.

Another work investigated the effect of metal additives to Raney nickel on the methanation reaction (23). They studied the effect of low level additions of B, Ce, Co, Mn, Mo, Pd, Re, Ti, Y, Zn and Zr on methanation activity and resistance to hydrogen sulfide poisoning. They prepared fused alloys by arc melting. Each alloy was examined metallographically to detect the phase or phases present. Catalysts were prepared by leaching the powdered alloy with NaOH solution. This made the active catalyst which they studied. Surface site measurements were made by hydrogen adsorption, assuming one hydrogen atom per active metal site.

Activity of the catalysts was measured by measuring the rate of methanation at 320°C and atmospheric pressure with a reactant gas mixture of 1 part carbon monoxide, 8 parts hydrogen, and 991 parts helium.

A problem which occurred from melting the alloys and leaching the alloys to form the active catalysts was the loss of some or most of the low level additive.

They found that Co, Ti, Y and Zn addition improved the resistance to hydrogen sulfide poisoning but only addition of Co improved the rate of methanation when compared to the Raney nickel catalyst.

In a study by D. J. Elliot, ruthenium and ruthenium mixed with nickel and copper supported on faujasite zeolites (type Y), catalysts were studied (24). He varied the atomic percent of ruthenium over the following ranges: 100%, 80%, 49%, 19%, 13% and 0.0%. His reaction conditions were 280°C, 150 Torr carbon monoxide, and 450 Torr hydrogen. He observed that the turnover numbers for their ruthenium-nickel catalysts changed linearly with varying composition of ruthenium. From Shunk, these two metals are virtually immiscible (25). We surmise that no alloy was formed on the surface of the support, but that the metals existed as separate particles of metal, with little interaction between ruthenium and nickel.

For the ruthenium-copper system, he varied the atom percent ruthenium over the following ranges: 100%, 82%, 76%, 51% and 14%. Under the same reaction conditions, he observed that the turnover numbers decreased rapidly upon addition of copper, similar to what was observed by Araki and Ponoc for a copper and nickel thin film system (18). Copper appears to dilute the number and decrease the size of active ruthenium clusters. From Hansen, again these two metals are immiscible (17).

We have reviewed several studies on the hydrogenation of carbon monoxide over various metals, mixed metals and supports. It was decided to study a system in which the two metals were soluble in each

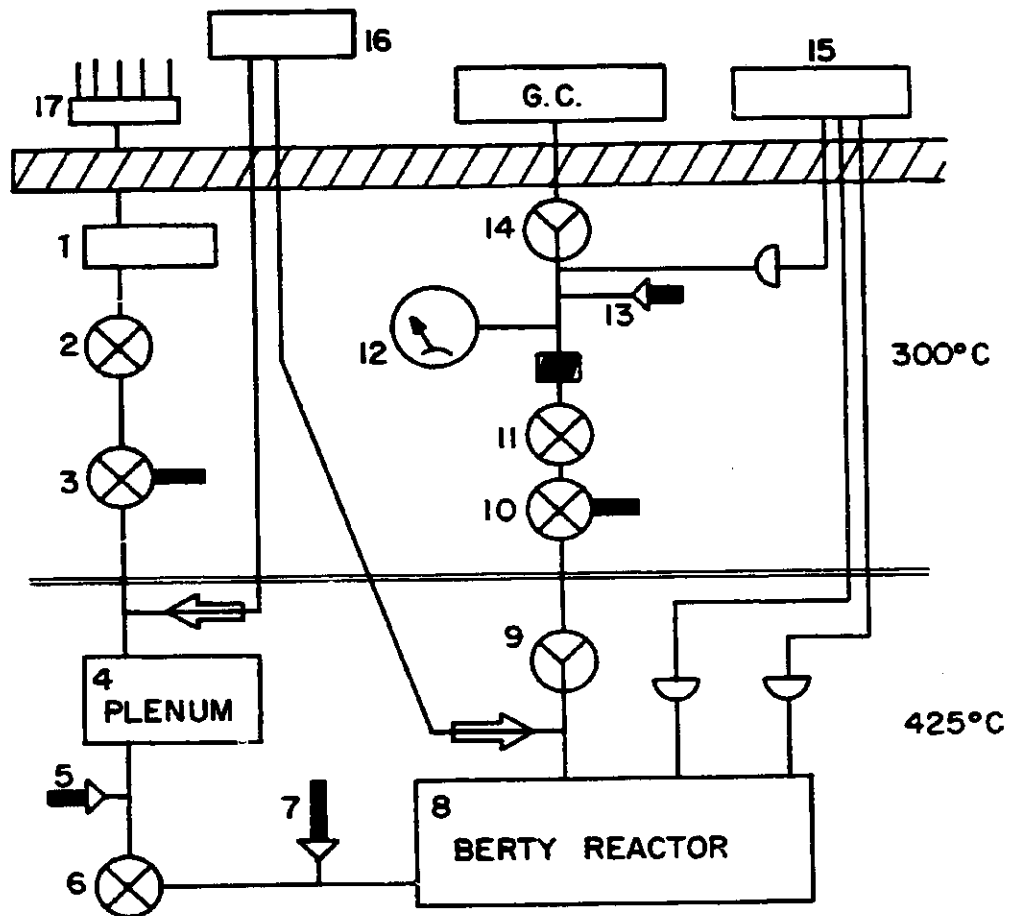
other. M. D. Slaughter recently completed a study of methanation on evaporated ruthenium films in our research group, providing local experience with this metal. Ruthenium is also the most active metal for this reaction. Hence, ruthenium was selected as a primary constituent. We decided to use alumina for support material because of its stability and relative promotion for the reaction under study. We chose rhenium because, like ruthenium, it is an active catalyst (however, less active) for the hydrogenation of carbon monoxide (26). Also, ruthenium and rhenium form a continuous series of solid solutions over all concentration ranges (27). This system, ruthenium-rhenium supported on alumina, was chosen for this study.

EXPERIMENTAL

We studied the hydrogenation of carbon monoxide over ruthenium, rhenium, and ruthenium-rhenium on alumina catalysts. The kinetics of the reaction were studied at conditions of 35 to 40 atmospheres total pressure and 205 to 235°C for the ruthenium and ruthenium-rhenium catalysts and 230 to 255°C with the same pressures for the rhenium catalyst.

Materials

This reaction was studied in a system (Fig. 2 and Table 3) which was built around a standard Bertly reactor from Autoclave Engineers, Inc. (Erie, PA). This reactor was rated for 3700 psi at 340°C. Included was also a magnetic drive impeller for mixing the reactant mixture and an electric furnace which would heat the reactor to 500°C. Other parts of the system were a reaction vessel, a two channel digital pressure indicator, and an air driven booster compressor. The reaction vessel (plenum) was rated at 11,950 psi at 38°C from American Instrument Company (Aminco). This was used to mix the reactant gases prior to releasing them to the catalyst chamber. The two channel digital pressure indicator with two 5000 psi air cooled transducers from Autoclave Engineers, Inc. was used to determine pressures of the gases. The air driven booster compressor (Haskell, Norman Equipment Co., Cedar Rapids) was used to pressurize the gases, which were fed from pressurized cylinders through a manifold assembly. On-off, rupture, and micro-metering valves for control of gases were purchased from Autoclave



SYMBOL	MEANING	SYMBOL	MEANING
⊗	VALVE	▬	TO EXHAUST
⊙	LEAK VALVE	—D—	THERMOCOUPLE
←	MANOMETER	▨	WALL
⬅	RUPTURE VALVE		

Figure 2. Schematic of system used in this study

Table 3. A key for Figure 2

Number	Meaning
1	compressor
2	2-way 2-on pressure valve
3	3-way 2-on pressure valve
4	plenum chamber
5	rupture valve
6	2-way high temperature pressure valve
7	rupture valve
8	Autoclave Berty reactor
9	micrometering valve
10	3-way 2-on pressure valve
11	2-way 2-on pressure valve
12	pressure gauge
13	rupture valve
14	Varian leak valve
15	temperature controller or voltmeter
16	pressure indicator
17	manifold

Engineers. A variable leak valve from Varian Vacuum (Park Ridge, IL) was used for fine control of the effluent stream during reduction of catalysts and during surface site measurements. A six inch diameter pressure gauge, with a range of 0-600 psi (O. W. Heyman Co., Inc., Cleveland, OH), was used to monitor the pressure of the effluent gases. The electric furnace supplied with the Bertly reactor was composed of three resistance elements. Each zone was powered by a variac. One variac was set and operated continuously while the other two were relay controlled by a temperature controller (Love Controls Corp., Wheeling, IL). This controller received temperature input from a type K (Chromel-alumel) thermocouple located at the bottom of the catalyst bed.

Gases used in the experiments were hydrogen (99.95% pure) and nitrogen (99.999% pure) from Union Carbide and carbon monoxide (technical grade 99.0% min.) and methane (ultra-high purity 99.97%) from Matheson. These gases were used without any further purification.

Catalysts were prepared from RuCl_3 , Re_2O_7 and gamma alumina ($100 \text{ m}^2/\text{g}$) obtained from Alpha Ventron.

For analysis of the hydrocarbon products, we used a Varian 3740 gas chromatograph (Park Ridge, IL). This instrument was equipped with dual flame ionization detectors and a dual gas sampling valve, plumbed for simultaneous injection. Two columns were used, a 6' x 1/8" stainless steel column packed with 5% OV-101 on chromosorb P and a 12' x 1/8" stainless steel column packed with 20% OV-101 on chromosorb P. A Perkin-Elmer 820 gas chromatograph with a thermal conductivity detector was used to detect hydrogen, carbon monoxide, methane and nitrogen. Two

stainless steel columns, 2' x 1/8" packed with 5A molecular sieves from Union Carbide, were used for the separations.

A ruthenium-rhenium alloy (50:50 atom %) was studied in an Auger electron spectrometer built by Varian Associates (Palo Alto, CA). This instrument was capable of attaining pressures in the ultra-high vacuum range (10^{-9} to 10^{-10} Torr). The main thrust of this experiment was to determine if any surface segregation occurred. The alloy was prepared by arc melting the two metals to form a button. This button was then spark cut to form a sample of the correct size for the Auger instrument and then mechanically polished with 0.03 μm particle size Linde B alumina.

System Design

The kinetic experiments were carried out in a medium pressure reactor, a schematic of which is shown in Fig. 2, with Table 3 serving as a key. This system consisted basically of two parts. One, which contained the plenum (between valves 2 and 6) was used to pre-mix the reactant gases. The other contained the Berty reactor where the catalyst was placed and the reaction occurred. Part of the system (containing plenum and reactor) could be heated to 425°C and the rest of the system could be heated to 300°C. The reactor was equipped with three cylindrical inserts to be used for changing the size of the catalyst chamber. These inserts were also used to determine the volume of the plenum and reactor chambers. The volume displaced by these inserts was estimated by water displacement. The volume displaced by all three inserts was found to be 0.663 liters. We then conducted two series of expansion

experiments. First, we pressurized the plenum with nitrogen and allowed that to expand into the reactor with all three inserts in place. Then we repeated this without the inserts. This gave us two equations (10 and 11) and two unknowns which when solved gave us the volumes of our system's chambers. P_1 and P_3 are plenum

$$P_1 V_P + P_{ATM} V_R = P_2 (V_P + V_R) \quad (10)$$

$$P_3 V_P + P_{ATM} (V_R - V_i) = P_4 (V_P + V_R - V_i) \quad (11)$$

pressures before expansion. P_2 and P_4 are pressures after expansion, and V_P , V_R and V_i are volumes of plenum, reactor and inserts, respectively. We found the volume of the plenum to be 0.528 liters and the volume of the reactor to be 1.358 liters. Since the reactor was operated with all three inserts in place, this gave us a reaction volume of 1.223 liters.

When we started work on the system, it was not in operable condition. We dismantled and thoroughly cleaned the whole assembly of tubing and reaction vessels. After regrinding the pressure seal joints, the system was reassembled and tested for leaks.

We added plumbing so that we could flow gases through the reactor for reductions and surface site determinations. We also added an exhaust duct system to contain and flush gases from the room should one of the rupture valves release. We installed a temperature controller that would keep the reaction chamber to $\pm 7^\circ\text{C}$ of the set point temperature. The temperature varied in a sine wave manner so that if we started a countdown procedure at a certain point, we could duplicate

reaction temperatures to within $\pm 2^\circ\text{C}$. With these modifications, the system was capable of producing kinetic runs with consistent reproducible results.

Preparation of Catalysts

Catalysts were prepared by impregnating alumina with aqueous solutions of metal salt or oxide (RuCl_3 or Re_2O_7). The solution (0.6 ml/g alumina) was added dropwise from a buret to alumina pellets which were shaped like cylinders ($1/8'' \times 1/8''$). The pellets were then placed in an oven at 110°C to dry overnight. The ruthenium catalyst was then placed in the reactor and reduced in flowing hydrogen at 400°C for 8 hours. The rhenium and ruthenium-rhenium (impregnated successively) after drying were calcined at 225°C for 4 hours and then at 400°C for 4 hours. The catalysts were then placed in the reactor and reduced in flowing hydrogen at 400°C for 8 hours.

Analysis for metal content of the catalysts was performed by x-ray fluorescence. After the catalyst was dried, we leached the metal salts from the support. This was achieved by boiling a powdered sample for one hour in 50:50 (volume) concentrated hydrochloric acid and water, and then stored overnight. This solution was then filtered, placed in a volumetric flask and analyzed by x-ray fluorescence. Table 4 shows the results. We found, for our preparative technique, that the mixed metal catalyst contained 0.74% Re and 0.54% Ru. The powdered alumina residue which was filtered off from the solution was dried and analyzed for ruthenium and rhenium content. From Table 5, we see a comparison of these powders to the unimpregnated alumina and a ruthenium-rhenium

Table 4. Summary of x-ray fluorescence analyses to determine amount of metal on the catalyst

		Re 8640 eV Re L α		Ru 19220 eV Ru L α	
<u>Standards</u>					
	Concentration	Peak Area	Concentration	Peak Area	
A	0.436 g/l	102967	0.547 g/l	251889	
B	0.281 g/l	51211	0.274 g/l	123848	
C	0.109 g/l	25257	0.137 g/l	63086	
D	0.0545 g/l	13152	0.0684 g/l	31675	

<u>Unknowns</u>					
Wt. Sample	Re Peak Area x Attenuation	Concentration	Re Wt. %	Ru Peak Area x Attenuation	Ru Concentration
1 0.483 g	45585 x 2	0.386 g/l	0.80	65334 x 2	0.285 g/l
2 0.803 g	96345 x $\frac{20}{16}$	0.510 g/l	0.636	138768 x $\frac{20}{16}$	0.378 g/l
3 0.5446 g	49497 x 2	0.420 g/l	0.77	67843 x 2	0.296 g/l
					0.590
					0.471
					0.543

Table 5. X-ray fluorescence of powdered alumina after removal of metals from the catalyst

		Ru L α	% Ru	Re L α	% Re
	1	52,929	0.06	7,003	0.015
Ru-Re/Al ₂ O ₃ samples	2	74,171	0.085	8,308	0.015
	3	43,204	0.05	6,332	0.015
γ -Al ₂ O ₃	4	1,032	0.0	2,221	0.005
Standard	5	437,926	0.54	350,549	0.85

catalyst. We conclude that the salts were successfully removed from the support and that our catalyst loadings were acceptable.

Kinetics Procedure

The general procedure started with increasing the mixing speed to the desired RPM. Then the plenum was separated from the catalyst chamber by closing valve #6. We then pressurized the plenum to the desired pressure of carbon monoxide, hydrogen and nitrogen. This charge was released onto the catalyst. A leak from the catalyst chamber was then established and the effluent monitored for the amount of methane produced.

There are several things one must consider when conducting kinetics experiments. The reaction under study is very exothermic. If the reaction proceeds too rapidly, the temperature of the catalyst bed may change, giving invalid results. This may even give hot spots in the catalyst bed. To minimize this overheating problem, we have used a low weighting of metal, small charge of catalyst and have kept conversions of carbon monoxide to 5% or less. The Berty reactor mixes the reactant gases forcing them through the catalyst so that with each pass a small amount of carbon monoxide is converted. It was necessary to operate under conditions such that concentration gradient effects were minimal. This is accomplished by increasing the speed of the mixing fan while holding other variables constant (28). Eventually the rate of reaction will be independent of mixing speed. This speed was assumed for standard conditions for subsequent reactions. It was found that we could clean the catalyst by flowing hydrogen at reaction temperature for

approximately one half hour. This hydrogenated surface carbon to make methane. When the methane production reached a low level, we knew that our catalyst was clean. This cleaning procedure gave consistent reproducible results.

Next we conducted a standard kinetics study. There are basically three parameters to vary: temperature, pressure of hydrogen and pressure of carbon monoxide. By varying temperature while holding reactant gas pressures constant, we can construct a log rate vs. reciprocal temperature plot; if linear, its slope is the apparent activation energy divided by the gas constant and 2.3. Varying one reactant gas pressure and keeping the other gas pressure constant as well as temperature, one gets by plotting log rate vs. log pressure, a graph whose slope corresponds to the reaction order of the gas whose pressure was varied. In this way, we can probe into a particular reaction by experimentally determining E_a/R , X and Y in the following equation

$$\text{Rate} = A e^{-E_a/RT} P_{\text{CO}}^X P_{\text{H}_2}^Y \quad (12)$$

in which A is the pre-exponential factor, E_a is the apparent activation energy, R is the gas constant, X is the order with respect to carbon monoxide pressure, and Y is the order with respect to the hydrogen pressure.

Rates are expressed in molecules per site per second. This allows meaningful comparison with work of other authors. This necessitated measurement of the number of surface sites on our catalysts. We used a flow technique at atmospheric pressure and a reactor temperature of

300°C. We flushed the system thoroughly with nitrogen. This was followed by a dose of carbon monoxide which was then left for three hours to allow deposition of carbon to occur. Next was another nitrogen flush to get rid of carbon monoxide, followed by a slow flow of hydrogen. This produced a bell shaped curve, the area of which was approximated by a summation;

$$\mu \text{ moles CH}_4 \text{ total} = \sum_{i=1}^n \left(\frac{\mu \text{ mole CH}_4}{V \text{ ml}} \right)_i (F \text{ ml/min})_i \Delta t_i \text{ min} \quad (13)$$

where V = volume of injector, F = flow rate of hydrogen through reactor, and Δt is the time increment between injections. We assume one methane molecule to one metal surface atom. This gave us a good approximation of the number of metal surface sites present on our catalysts.

RESULTS AND DISCUSSION

Surface Characterization of a Ru-Re Alloy by Auger Spectroscopy

We prepared a sample of 50:50 atomic percent ruthenium and rhenium by arc melting the metals eight times. This formed a bead which was spark cut to the desired size for the sample holder.

Standard conditions for taking Auger spectra were as follows: vacuum 5×10^{-9} Torr or better, beam current 6×10^{-7} Amp, beam energy 2 KV, and peak to peak modulation 5 V.

The initial spectrum is shown in Fig. 3a. The major peaks are rhenium at 33 eV, ruthenium at 151, 202, 232, 273 eV, oxygen at 517 eV, and carbon at 273 eV. The carbon and ruthenium peaks at 273 eV are superimposed. The top portion of the peak is due only to ruthenium and the bottom peak is due to carbon and ruthenium. One then can measure the amount of carbon present by taking a ratio of the two peaks. A clean ruthenium sample gives a ratio (upper to lower peak) of 0.75 to 0.80 (29). We will let this ratio be Q. We also used the ratio of the ruthenium 232 eV peak to the rhenium 33 eV peak. We let this ratio be R. This way we can quantitatively estimate the carbon present on the sample surface and the segregation of either metal to the surface.

Our cleaning procedure started with bombardment with hydrogen ions. Conditions were 1×10^{-5} Torr hydrogen, 20 mA current, and beam energy of 2.0 KV for 15 minutes. The beam was rastered over a 1 cm^2 area. We then tried to remove the carbon by successively heating in oxygen and hydrogen. This required care, for if we

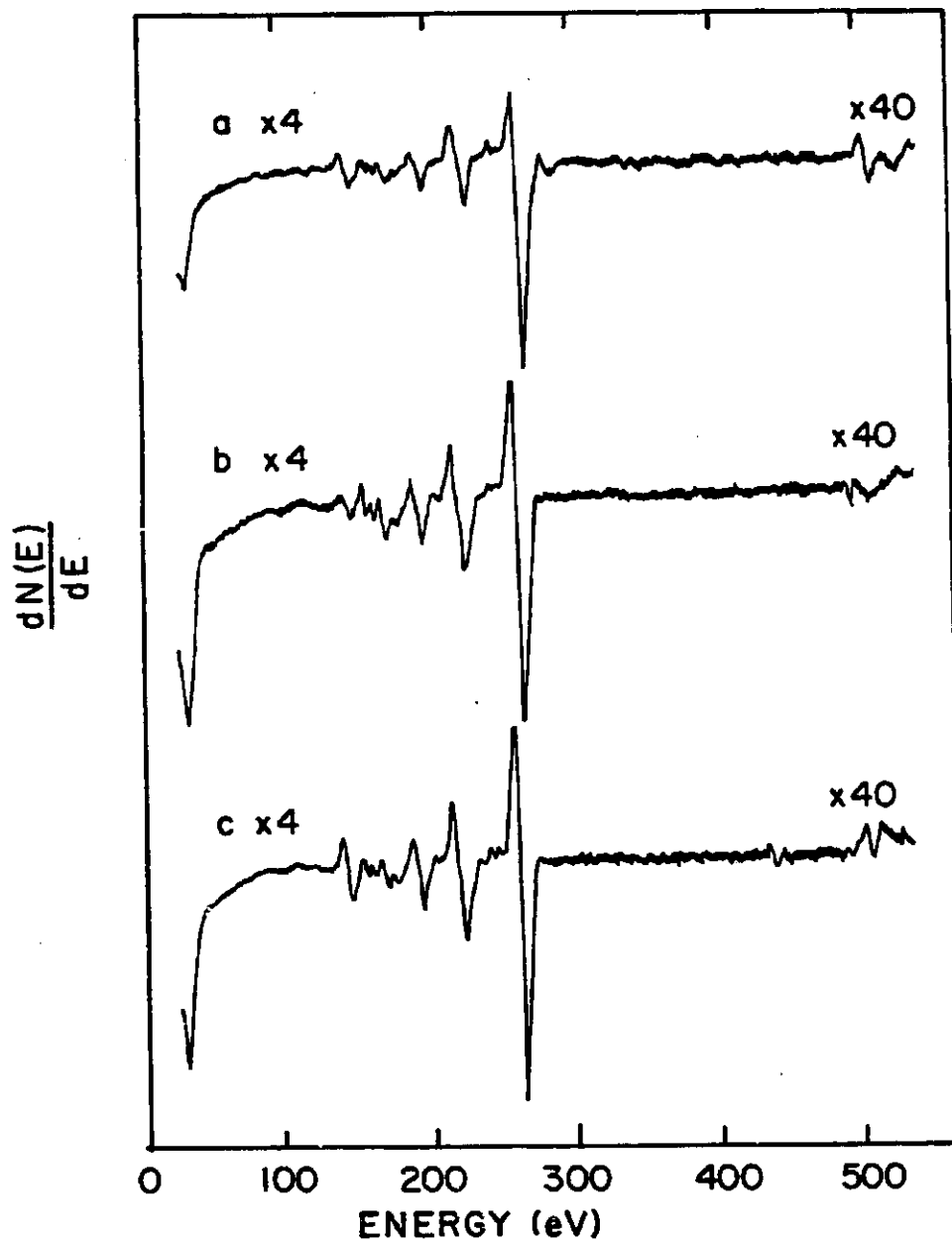


Figure 3. Auger spectra of a Ru-Re alloy. a) initial spectrum, b) after hydrogen ion bombardment and c) after nine heating in oxygen, then hydrogen cycles

heated the sample too much, one of the constituents might segregate to the surface, destroying the possibility of obtaining a clean undisturbed spectrum. We needed to heat the sample, however, in order to remove the carbon. Our method of attack was to heat at lower temperatures noting any change in the spectrum. We then would gradually heat to higher temperatures. For carbon removal, we heated to 370°C in 1×10^{-5} Torr oxygen for five minutes followed by heating to 370°C in 1×10^{-5} Torr hydrogen for five minutes. This was supposed to get rid of surface carbon. After a total of nine cycles, carbon was still present; the ratio Q was never better than 0.65 (Fig. 3c).

Next we heated the sample in vacuum to 800°C for 30 minutes. Upon cooling to room temperature, we took the spectrum shown in Fig. 4a. The Q ratio shows that carbon is still present and the R ratio is approximately the same as R ratios from other spectra, showing that no surface segregation had occurred. We heated the sample to 760°C in 1×10^{-5} Torr oxygen for 30 minutes to see if this might remove the carbon. This produced the spectrum shown in Fig. 4b. Carbon was still present, indicated by a value of $Q = 0.374$. This was followed by five cycles of heating in oxygen and then hydrogen. Still we see that carbon is present ($Q = 0.50$) and that the R ratio shows no appreciable change (Fig. 4c). Figure 5a shows a spectrum of the alloy after heating to 825°C in vacuum for two hours. Still, we see little change. Figure 5b shows the alloy after heating in vacuum for three hours at 1000°C. Again carbon is present ($Q = 0.676$) and there is little change in the R ratio ($R = 0.113$). These results are summarized in Table 6.

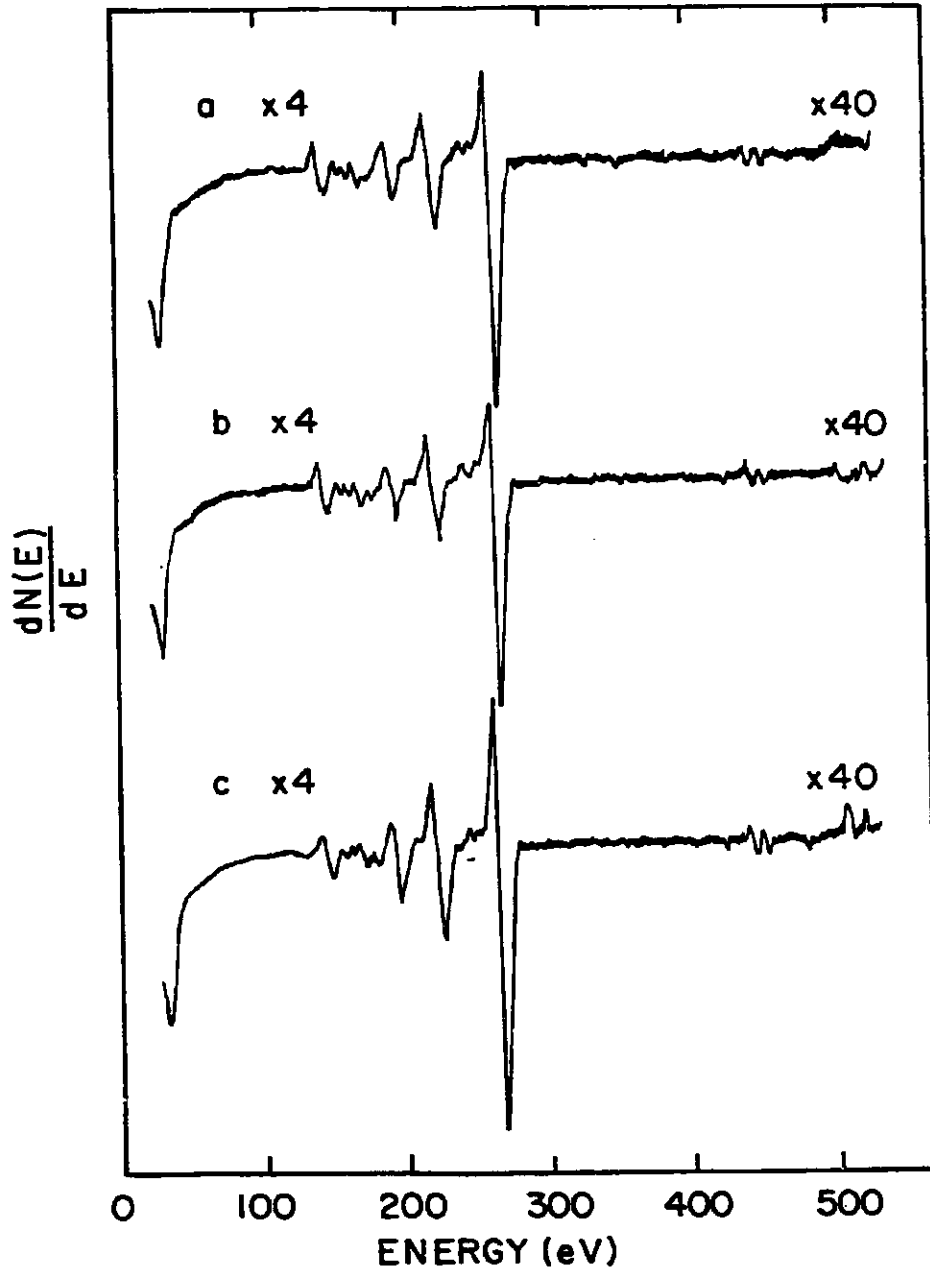


Figure 4. Auger spectra of a Ru-Re alloy. a) after heating to 800°C for 30 min., b) oxygen dose and heating to 760°C for 30 min. and c) after 5 cycles of heating in oxygen and hydrogen

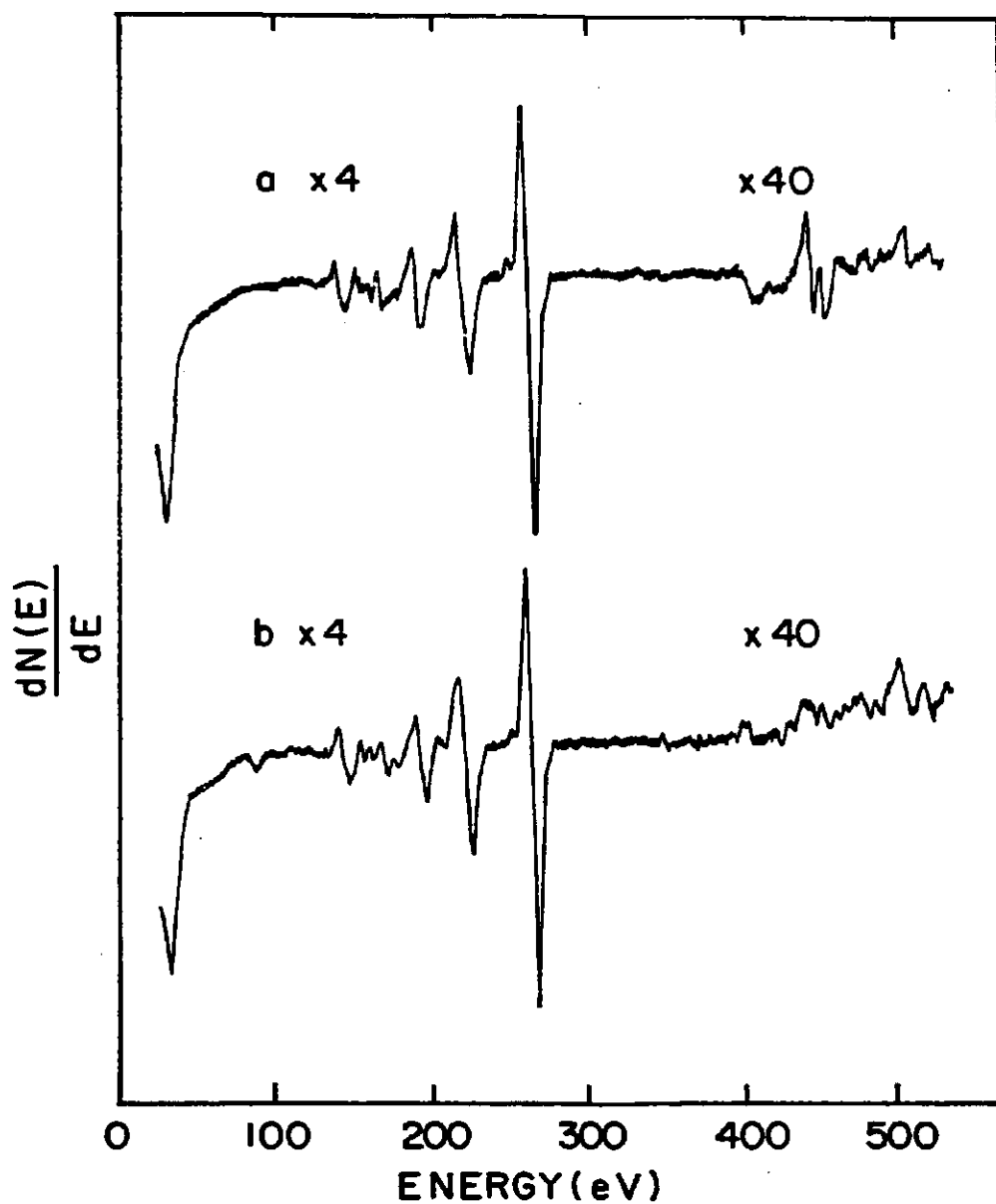


Figure 5. Auger spectra of a Ru-Re alloy. a) after heating in vacuum at 825°C for 2 hours and b) after heating in vacuum at 1000°C for 3 hours