Table 6. Summary of Auger analysis of a 50:50 atom percent ruthenium-rhenium alloy

Figure #	History	R	Q
3a	initial spectrum	0.100	0.344
3b	hydrogen ion bombardment, 15 min.	0.0878	0.637
3c	9 O_2/H_2 and heat cycles	0.0903	0.389
4a	heat to 800°C for 30 min.	0.0619	0.353
4b	O_2 and heat to 760°C for 30 min.	0.0721	0.374
4c	5 O_2/H_2 and heat cycles	0.101	0.500
5a	heat in vacuum for 2 hrs. at 825°C	0.102	0.650
5b	heat in vacuum for 3 hrs. at 1000°C	0.113	0.676
6a	heat in vacuum one week at 1050°C	0.127	0.695
6b	hydrogen ion bombardment, 15 min.	0.0615	0.433
7a	heat in vacuum one week at 1050°C	0.117	0.692
7b	hydrogen ion bombardment, 15 min.	0.102	0.576

At this point, we conclude the following:

1) treatment so far has produced no evidence for the segregation of either metal to the surface.

2) the carbon present is of a permanent form, i.e., a metal carbide.

We propose that this carbide originated from arc melting of the sample during its preparation. Some residual oil in the system may have combined with the metals to form a stable carbide.

Next we heated the sample in vacuum for one week at 1050°C. After cooling to room temperature, we took the spectra shown in Fig. 6a. Note the appearance of a peak at 92 eV. This is a silicon peak. We could remove this by bombardment with hydrogen ions for 15 minutes (Fig. 6b). We still see carbon on the surface (Q = 0.433) and see little change in the R ratio (R = 0.0615).

We then heated the sample in vacuum at 1050°C for another week. Figure 7a shows a spectrum after this treatment. Note that silicon (92 eV) has again diffused from the bulk. Figure 7b shows the sample after cleaning by bombardment with hydrogen ions for 15 minutes. We still have carbon on the surface (Q = 0.576) and we see no evidence for surface segregation by either metal.

We conclude that since there is no surface segregation observed by our Auger experiments, even with heating to 1050°C for two weeks, our conditions for reduction of the mixed metal catalyst would not lead either metal to segregate to the surface of the catalyst. We postulate that our mixed metal catalyst has a random distribution of ruthenium and rhenium atoms. We predict that the surface atoms are also randomly

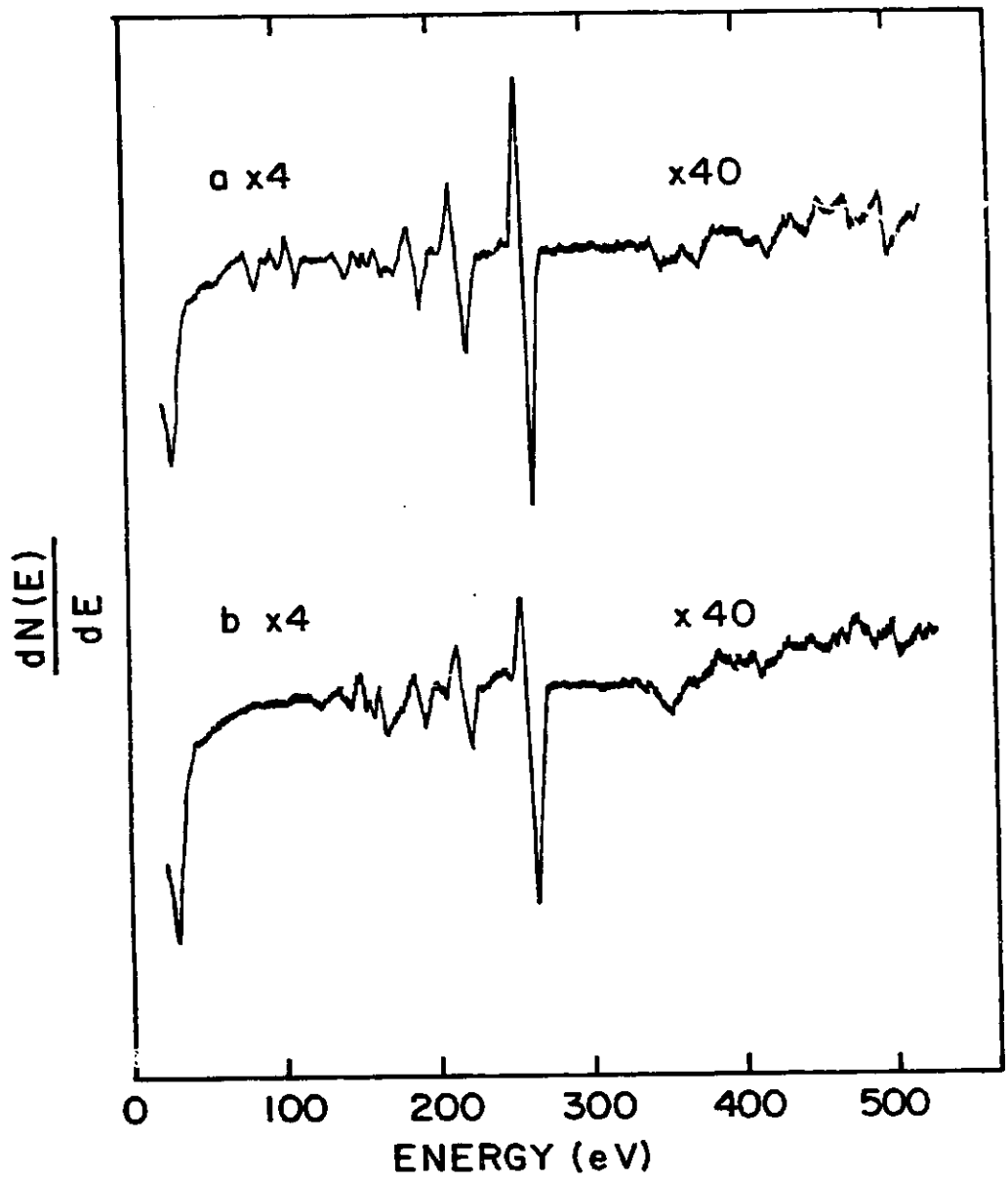

Figure 6. Auger spectra of a Ru-Re alloy. a) after heating in vacuum at 1050°C for one week and b) after hydrogen ion bombardment for 15 min.

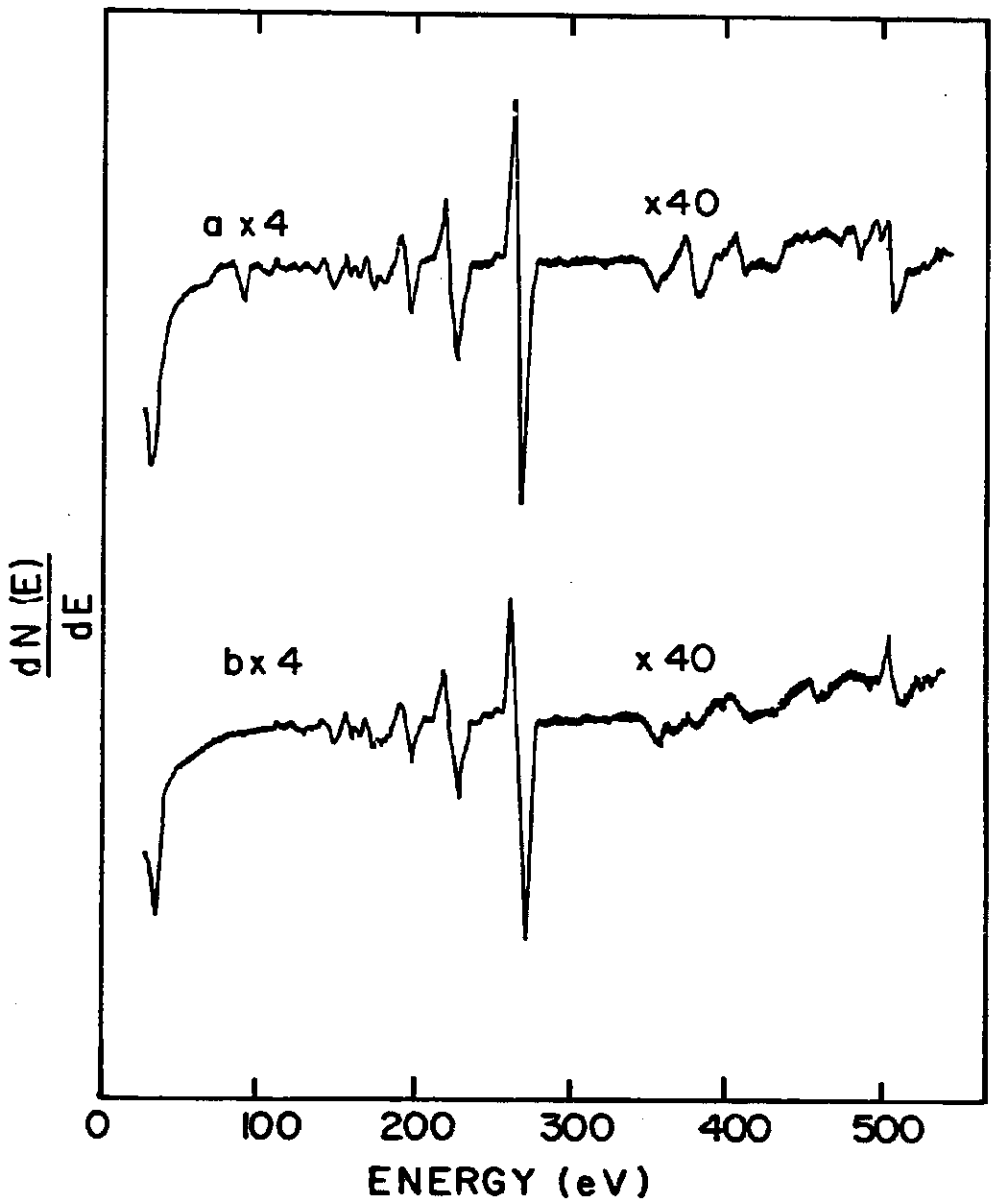

Figure 7. Auger spectra of a Ru-Re alloy. a) after heating in vacuum at 1050°C for a second week and b) after hydrogen ion bombardment for 15 min.

distributed because no segregation to the surface of either constituent will occur.

Results of Kinetics Study

We investigated the methanation reaction over Ru/Al_2O_3, Re/Al_2O_3 and $Ru\text{-}Re/Al_2O_3$ catalysts. Operating conditions are 200°C to 260°C and 35 atm. to 40 atm. for these kinetic runs. The major product from these reactions was methane with small amounts of higher hydrocarbons. The pressures of carbon monoxide and hydrogen were varied by factors of three or four. Initial rates were measured throughout this work. Conversions of carbon monoxide were usually below 5%. The hydrogen to carbon monoxide ratio was always greater than three, favoring the production of methane. The data are presented in conventional log rate vs. log pressure plots. All of our curves were approximately linear, which is to be expected of higher pressure work over the pressure ranges we used. The slope of a curve represents the kinetic order of the reaction with respect to that reactant.

A plot of log rate vs. reciprocal temperature, if linear, has a slope equal to the apparent activation energy divided by the gas constant and 2.303.

Results of surface site measurements are shown in Table 7. We calculated dispersion (D) from Eq. (14).

$$D = \frac{\text{metal atoms on the surface}}{\text{total metal atoms}} \qquad (14)$$

If we suppose the crystallites cubes of diameter d, the area A, and volume V of each cube are given by

Table 7. Results of surface site measurements

Catalyst	Weight (g)	wt. % Metal	Surface Sites (μ mole)	Dispersion (%)	Surface Area (m^2/g)	Crystallite size $\bar{d}$ (Å)
Ru/Al_2O_3	17.33	0.54	484.3	52.3	281.3	30.7
Re/Al_2O_3	52.66	1.51	684.2	16.0	50.4	103
Re/Al_2O_3	49.90	1.51	535.9	13.2	41.6	125
$Ru\text{-}Re/Al_2O_3$	12.80	0.54-0.74	342.5	28.5	--	--
$Ru\text{-}Re/Al_2O_3$	17.90	0.54-0.74	452.3	26.9	--	--
$Ru\text{-}Re/Al_2O_3$	16.44	0.54-0.74	500.1	31.9	--	--

$$A = 6d^2 \quad , \tag{15}$$

$$V = d^3 \tag{16}$$

Dispersion can be expressed as surface area over volume, or

$$D \times \frac{\text{atoms per unit volume}}{\text{atoms per unit area}} = \frac{A}{V} \quad . \tag{17}$$

Turn to Appendix II for completion of this derivation. We find for the average crystallite size

$$d = \frac{6\ a_o}{D} \tag{18}$$

where a_o is the atomic diameter (unit cell length).

The ruthenium catalyst was well-dispersed, which is usual, while the rhenium catalysts were less so. The mixed metal catalyst's dispersions were approximately midway between the dispersions of the single metal catalysts.

Kinetic data are presented for the Ru/Al_2O_3 catalyst in Figs. 8 to 10. Kinetic data for the Re/Al_2O_3 catalyst are shown in Figs. 11 to 13, and for the $Ru\text{-}Re/Al_2O_3$ catalyst in Figs. 14 to 16.

These results as well as some results from the literature are tabulated in Table 8. Values from the literature for the order with respect to hydrogen vary from 0.5 to 1.75 and with respect to carbon monoxide vary from 0 to -1.0. Our results are within these ranges.

Our activation energies are higher than those reported by most authors; that of Randhava et al. (30) is closest to ours.

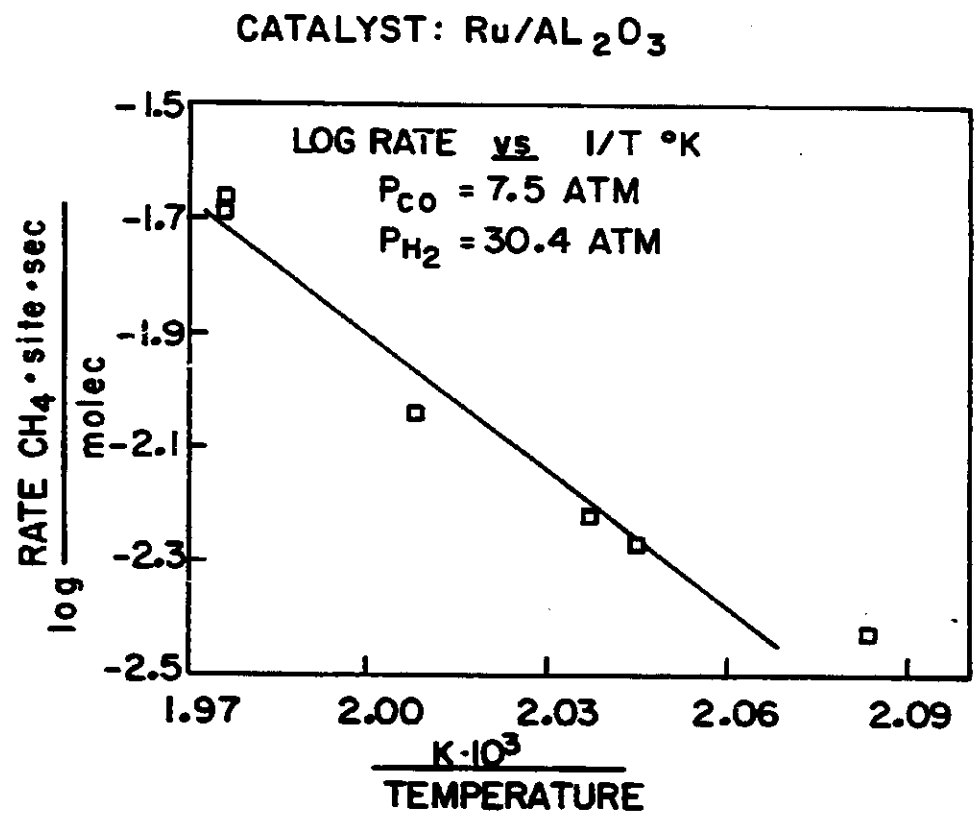

Figure 8. Variation of methanation rate with temperature plot for Ru/Al_2O_3

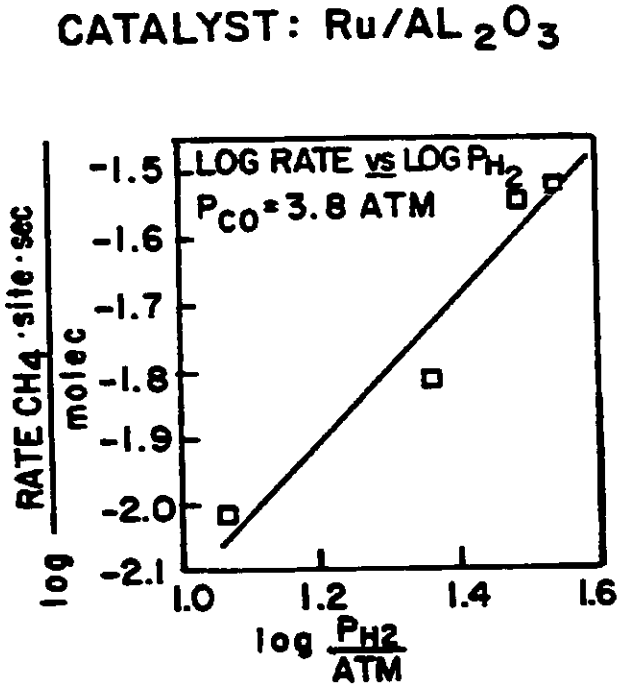

Figure 9. Order plot for variation of methanation rate with hydrogen pressure for Ru/Al_2O_3

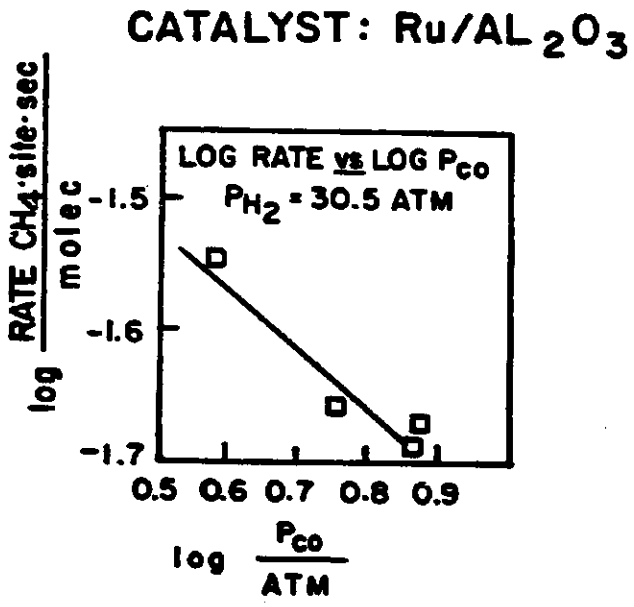

Figure 10. Order plot for variation of methanation rate with carbon monoxide pressure for Ru/Al_2O_3

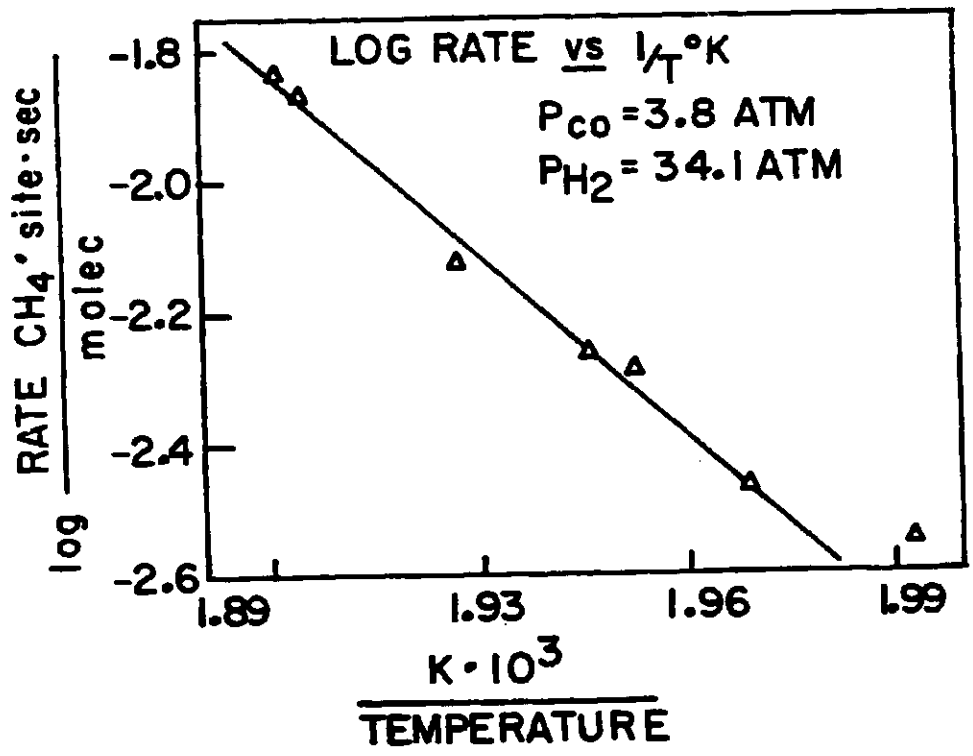

Figure 11. Variation of methanation rate with temperature plot for Re/Al_2O_3

CATALYST: Re/AL_2O_3

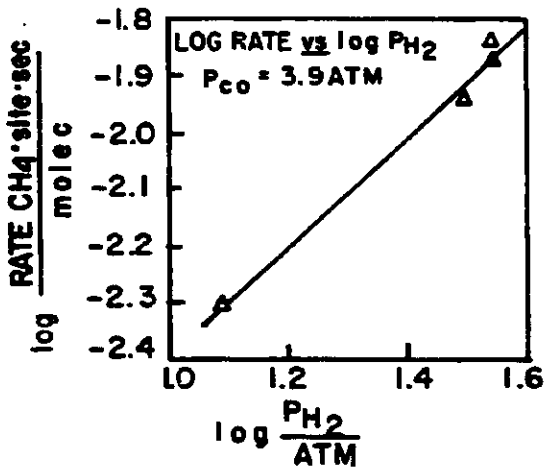

Figure 12. Order plot for variation of methanation rate with hydrogen pressure for Re/Al_2O_3

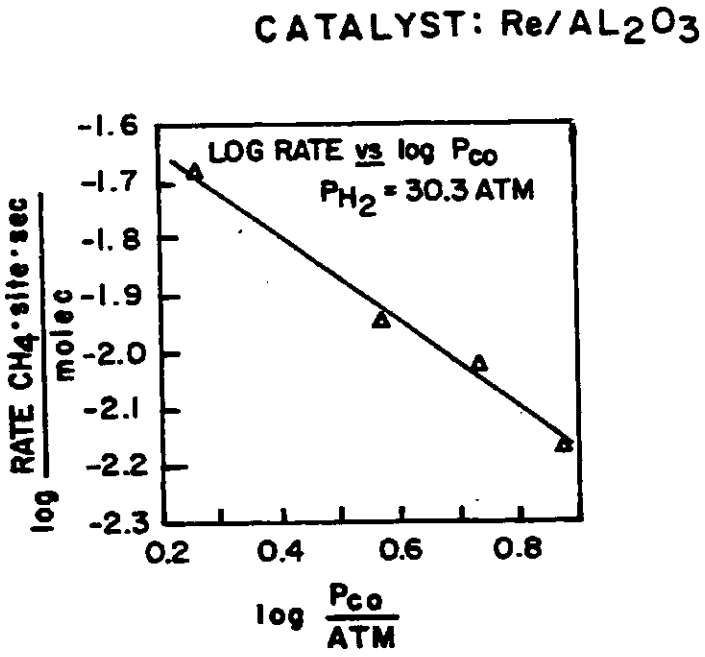

Figure 13. Order plot for variation of methanation rate with carbon monoxide pressure

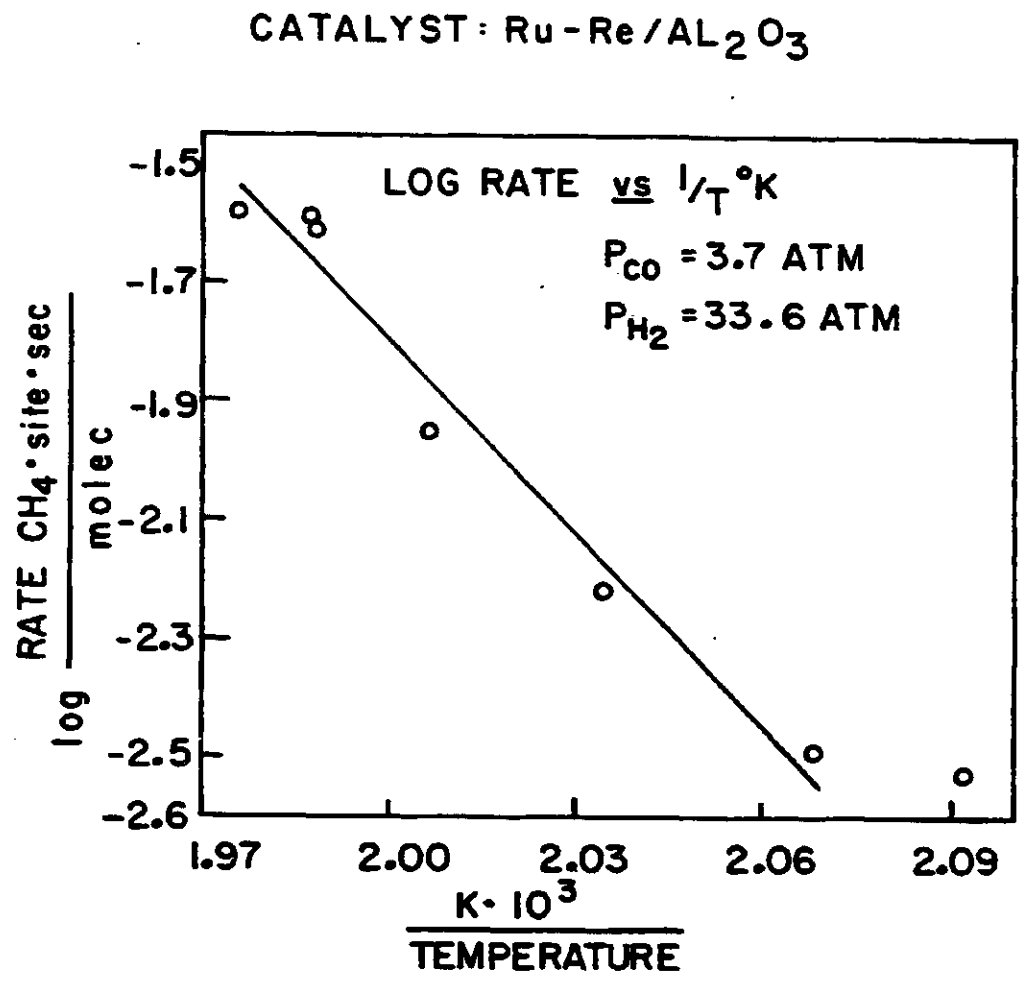

Figure 14. Variation of methanation rate with temperature plot for Ru-Re/Al_2O_3

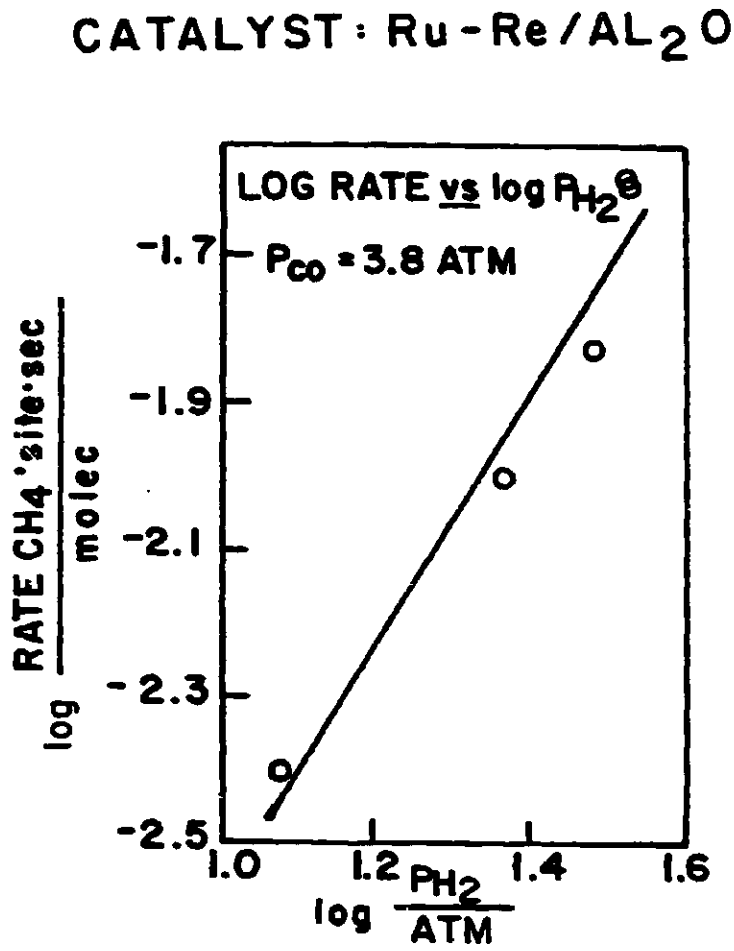

Figure 15. Order plot for variation of methanation rate with hydrogen pressure for Ru-Re/Al_2O_3

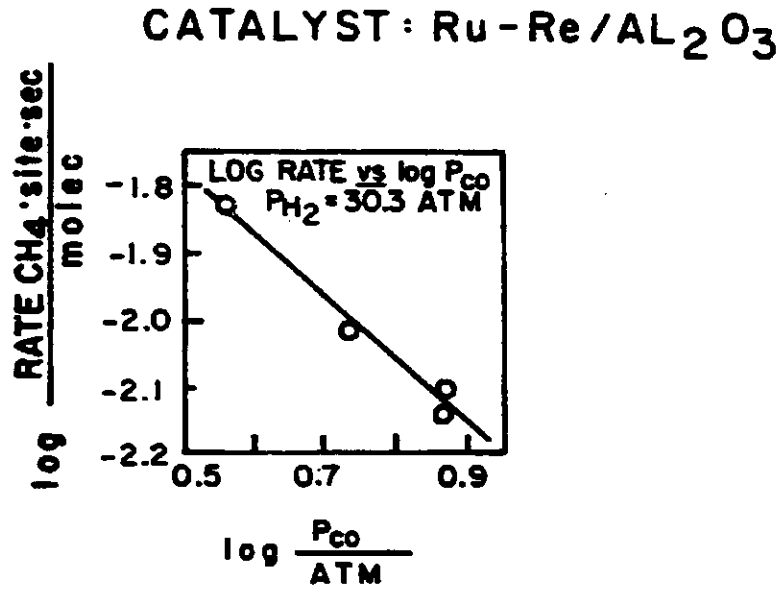

Figure 16. Order plot for variation of methanation rate with carbon monoxide pressure for $Ru-Re/Al_2O_3$

Table 8. Summary of rate expression parameters

$$\text{Rate } CH_4 = A\, e^{-Ea/RT}\, P_{CO}^{X}\, P_{H_2}^{Y}$$

Catalyst	P (atm)	Ea ($\frac{kcal}{mole}$)	X	Y	A ($\frac{molec}{site \times sec}$)	Ref.
0.54% Ru/Al_2O_3	38	39.3	-0.44	1.09	1.29×10^{14}	this study
1.51% Re/Al_2O_3	38	41.6	-0.77	0.98	2.33×10^{14}	this study
0.54% Ru - 0.74% Re on Al_2O_3	38	49.2	-0.97	1.73	4.69×10^{17}	this study
5% Ru/Al_2O_3	1	24.2	-0.6	1.6	5.7×10^{8}	12
0.5% Ru/Al_2O_3	1	37.2	--	--	---	30
1.5% Ru/Al_2O_3	1	24.0	-1.14	1.79	3.1×10^{4}	31
1.0% Re/Al_2O_3	1	23.0	--	--	---	26

Next we tried to fit equations (rate laws) to our experimental data. For the ruthenium and rhenium catalysts, we fit the data to the following equation:

$$\text{Rate } CH_4 = \frac{K_1 P_{CO} P_{H_2}}{(1 + K_2 P_{CO})^2} \quad . \tag{19}$$

When this is rearranged for linear plotting, it becomes

$$\left(\frac{P_{CO} P_{H_2}}{\text{Rate } CH_4} \right)^{1/2} = K_1^{-1/2}(1 + K_2 P_{CO}) \quad . \tag{20}$$

Plots based on this relation for the ruthenium and rhenium catalysts are shown in Figs. 17 and 18. For the mixed metal catalyst, we fit the data to this equation

$$\text{Rate } CH_4 = \frac{K_1 P_{CO} P_{H_2}^2}{(1 + K_2 P_{CO})^2} \quad . \tag{21}$$

When rearranged for linear plotting, this becomes

$$P_{H_2} \left(\frac{P_{CO}}{\text{Rate } CH_4} \right)^{1/2} = K_1^{-1/2}(1 + K_2 P_{CO}) \quad . \tag{22}$$

A plot based on this relation for the Ru-Re mixed catalyst is shown in Fig. 19.

From these linear plots, we determined the rate law constants K_1 and K_2 for all three catalysts. They are listed in Table 9.

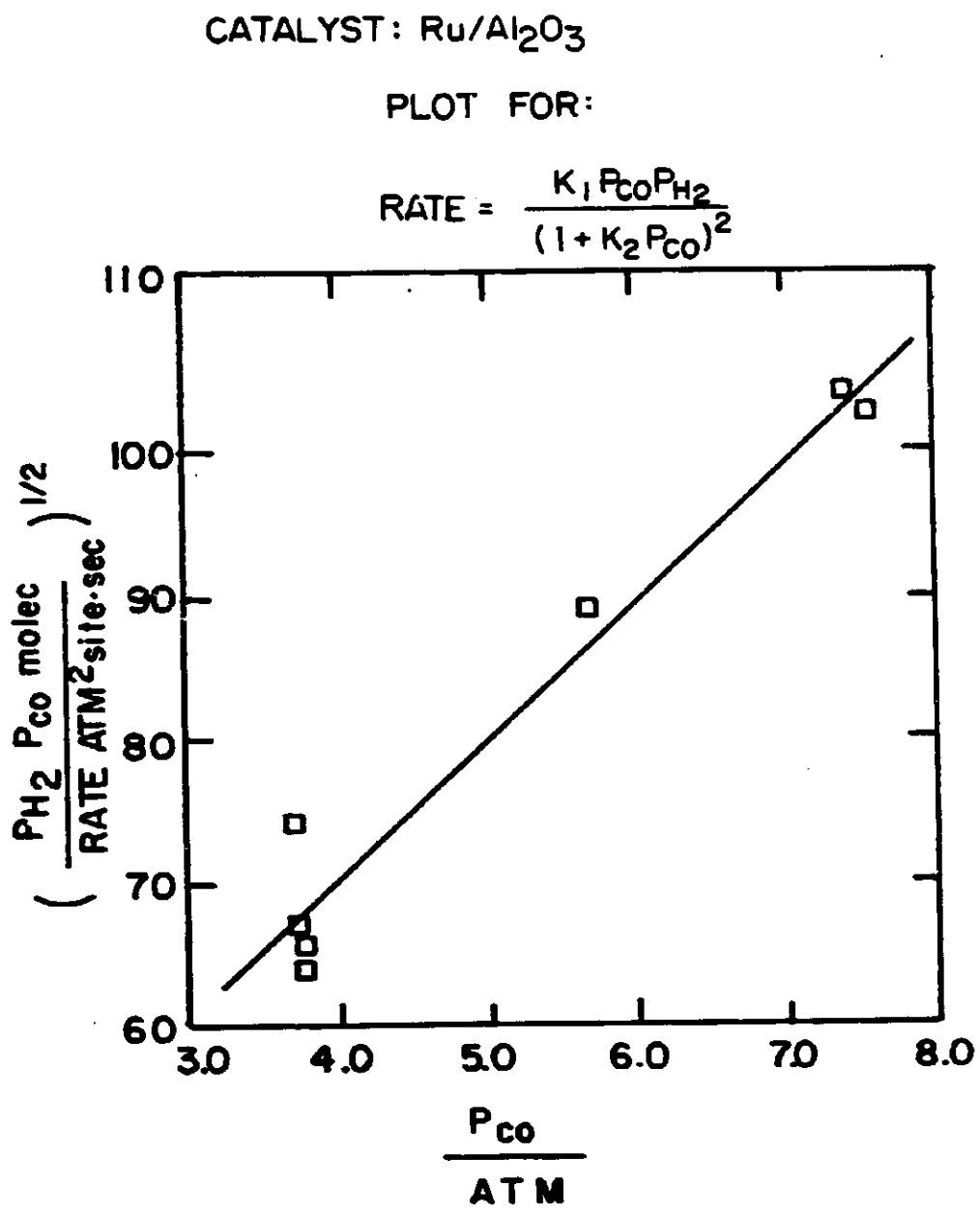

Figure 17. Linear plot for methanation data from the ruthenium catalyst

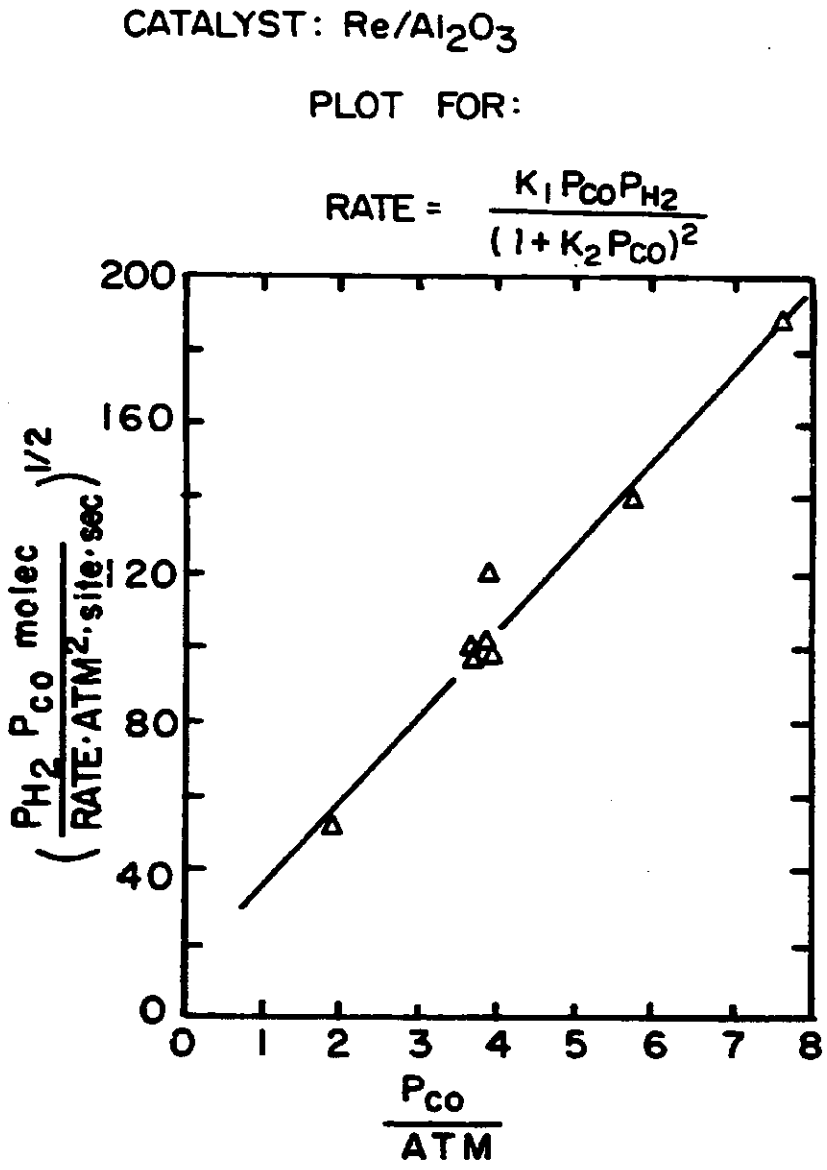

Figure 18. Linear plot for methanation data from the rhenium catalyst