

CATALYST: Ru-Re/Al₂O₃

PLOT FOR:

$$\text{RATE} = \frac{K_1 P_{\text{CO}} P_{\text{H}_2}^2}{(1 + K_2 P_{\text{CO}})^2}$$

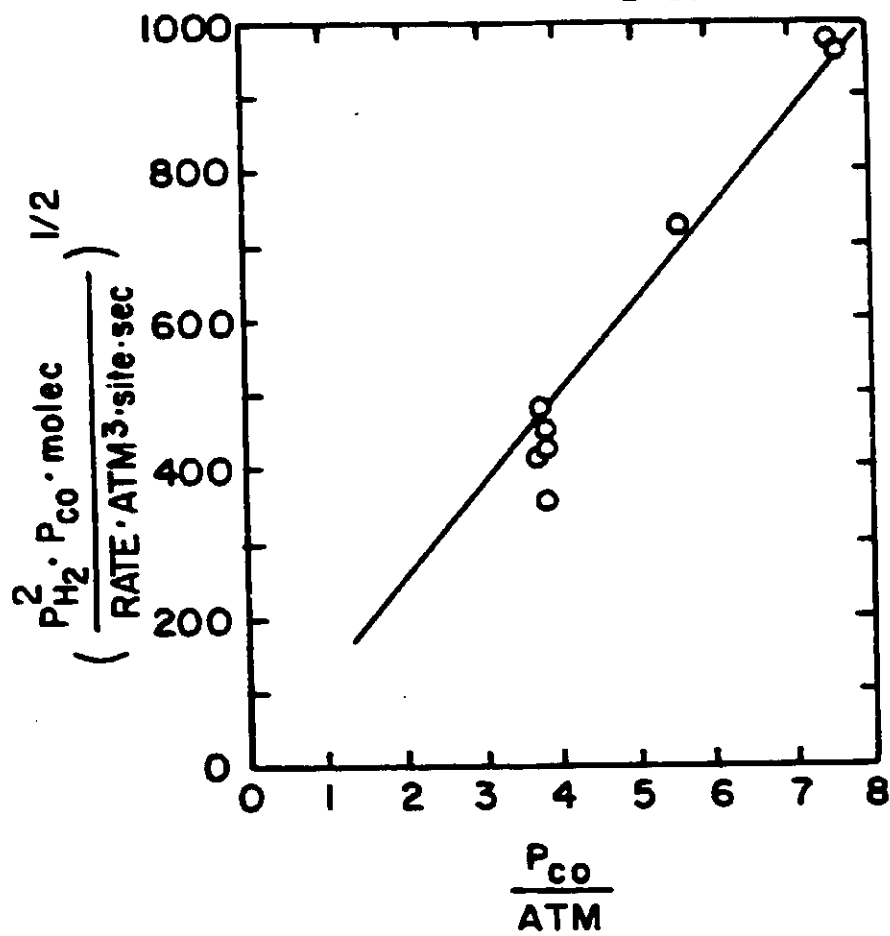


Figure 19. Linear plot for methanation data from the ruthenium-rhenium mixed metal catalyst

Table 9. Values of rate constants K_1 and K_2

Catalyst	K_1 ($\frac{\text{molec}}{\text{site} \times \text{sec} \times \text{atm}^2}$)	K_2 (atm^{-1})
Ru/Al ₂ O ₃	1.06×10^{-3}	0.320
Re/Al ₂ O ₃	5.05×10^{-3}	1.60
Ru-Re/Al ₂ O ₃	$5.20 \times 10^{-3} \times \text{atm}^{-1}$	8.80

From these rate laws and constants, we calculated rates for the particular reactant pressures we used. These are displayed along with the original data in Figs. 20 to 22. We were quite satisfied with the fits our theory gave. We would like to point out, however, that these expressions might not describe this reaction at pressures differing markedly from those at which our reactions were run.

Mechanistic Considerations

We attempted to develop a mechanism that is quantitatively consistent with our kinetic data. We will use a Langmuir-Hinshelwood type of approach (Appendix I), that is, reactant gases adsorbing and then reacting on the catalyst surface (32). To make these derivations manageable, we used an approach developed by Kemball (33) which involves the establishment of some, but not all of the possible equilibria which might exist between gas and surface species and between different kinds of species on the surface. We will let * represent an active metal surface site, *H or H* represent a hydrogen atom adsorbed on a site, and *CO represent an undissociated carbon monoxide molecule bonded by a double bond to a surface site. Other intermediate structures will be defined later.

Slaughter (29) in a very low pressure study of the methanation reaction on ruthenium thin films found the reaction orders with respect to both methane and water were zero. We will assume that this is true for our case.

It is necessary to consider the possibility of other reactions occurring at the same time as the reaction under study. Of reactions

CATALYST: Ru/Al₂O₃

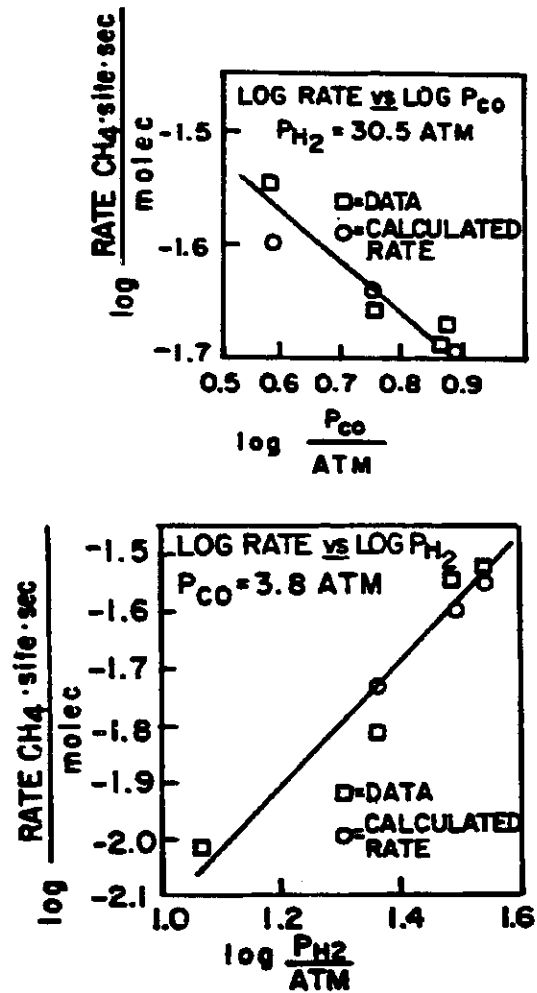


Figure 20. Plot of calculated methanation rates for the Ru/Al₂O₃ catalyst

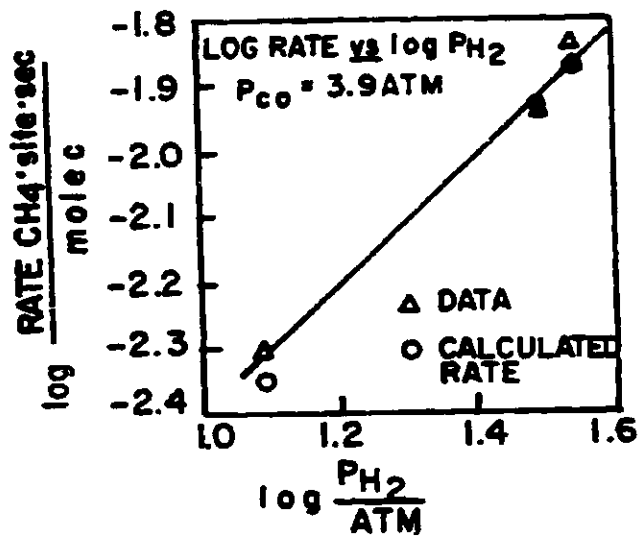
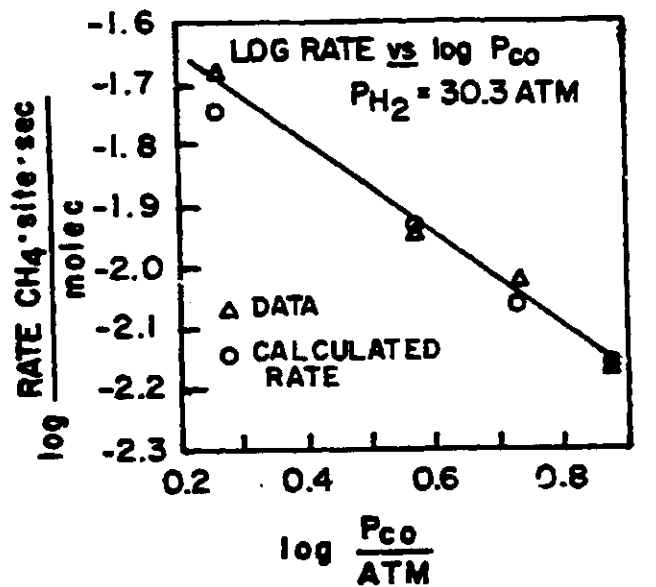
CATALYST: Re/AL₂O₃

Figure 21. Plot of calculated methanation rates for the Re/Al₂O₃ catalyst

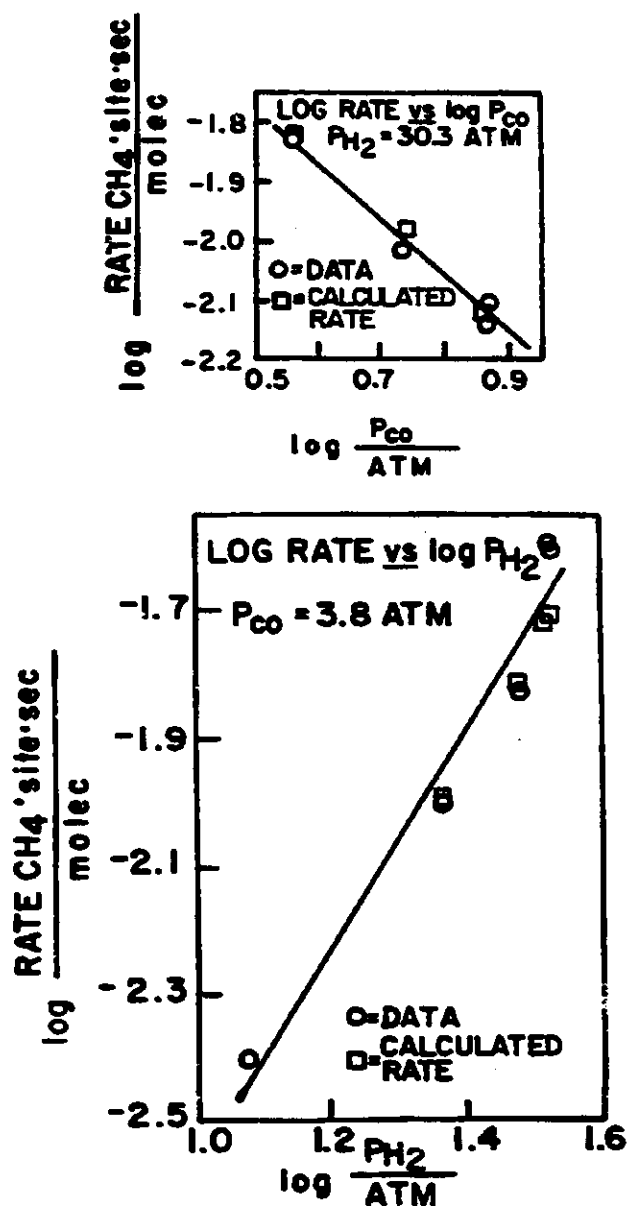
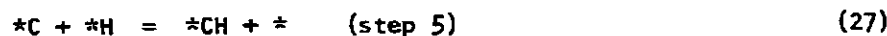
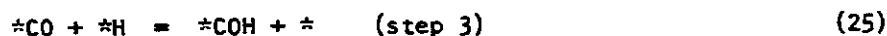
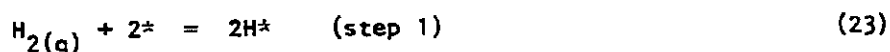
CATALYST: Ru-Re/AL₂O₃

Figure 22. Plot of calculated methanation rates for the Ru-Re/Al₂O₃ catalyst

(5), (6) and (7), only the water gas shift reaction (5) needs consideration. For ruthenium, the water gas shift reaction does not occur appreciably at our reaction temperatures. For rhenium, it does occur under conditions of our reaction, but since we are only measuring the initial rates of reaction, the water partial pressure developed is too low for this reaction to occur appreciably (34).

We now proceed to develop a mechanism for methanation on the ruthenium and the rhenium catalysts. Consider the following sequence of elementary steps.



By the overall stoichiometry steps 4 and 8 must have the same rate. Steps 4 and 8 also go to completion. All other steps are equilibria. We now will develop expressions for each reaction intermediate.

$$K_1 = \frac{[H^*]^2}{[H_2][^*]^2} \rightarrow [H^*] = (K_1[H_2])^{1/2}[^*] \quad (31)$$

$$K_2 = \frac{[^*CO]}{[CO][^*]} \rightarrow [^*CO] = K_2[CO][^*] \quad (32)$$

$$K_3 = \frac{[^*COH][^*]}{[^*CO][H^*]} \rightarrow [^*COH] = K_3[^*CO][H^*]/[^*]$$

$$= K_3K_2[CO](K_1[H_2])^{1/2}[^*] \quad (33)$$

Because the rates of step 4 and step 8 must be equal,

$$k_8[^*CH_3][^*H] = k_4[^*COH][H^*] \rightarrow [^*CH_3] = \frac{k_4[^*COH]}{k_8}$$

$$= \frac{k_4K_3K_2[CO](K_1[H_2])^{1/2}[^*]}{k_8} \quad (34)$$

$$K_7 = \frac{[^*CH_3][^*]}{[^*CH_2][H^*]} \rightarrow [^*CH_2] = \frac{[^*CH_3][^*]}{K_7[H^*]} = \frac{k_4K_3K_2[CO][^*]}{k_8K_7} \quad (35)$$

$$K_6 = \frac{[^*CH_2][^*]}{[^*CH][H^*]} \rightarrow [^*CH] = \frac{[^*CH_2][^*]}{K_6[H^*]} = \frac{k_4K_3K_2[CO][^*]}{k_8K_7K_6(K_1[H_2])^{1/2}} \quad (36)$$

$$K_5 = \frac{[^*CH][^*]}{[^*C][H^*]} \rightarrow [^*C] = \frac{[^*CH][^*]}{K_5[H^*]} = \frac{k_4K_3K_2[CO][^*]}{k_8K_7K_6K_5K_1[H_2]} \quad (37)$$

The rate of formation of methane is then given by Eq. (38).

$$\text{Rate} = k_8[^*CH_3][^*H] = k_4K_3K_2[CO]K_1[H_2][^*]^2 \quad (38)$$

We will express surface site concentrations as fractional coverages, so their sum, including bare sites as well as sites occupied by reaction

intermediates, is unity.

$$1 = [*] + [*H] + [*CO] + [*COH] + [*C] + [*CH] + [*CH_2] + [*CH_3] \quad (39)$$

If we assume only bare sites and sites with carbon monoxide adsorbed have surface coverages appreciable compared to unity, Eq. (39) becomes

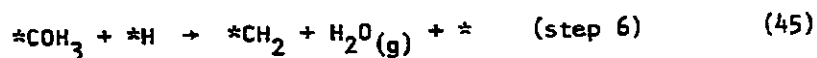
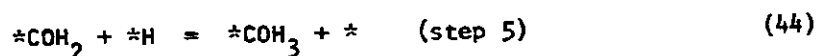
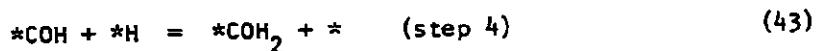
$$1 = [*] + [*CO] = [*] + K_2[CO][*] \quad (40)$$

$$[*] = \frac{1}{1 + K_2[CO]} \quad (41)$$

Now Eq. (38) becomes

$$\text{Rate} = \frac{k_4 k_3 k_2 [CO] K_1 [H_2]}{(1 + K_2 [CO])^2} \quad (42)$$

For the Ru-Re/Al₂O₃ catalyst, we propose to change steps 4 through 6 in the previous mechanism.



Now we have steps 6 and 8 going to completion. All other steps are in equilibrium. We calculate the expressions for the new intermediates as follows.

$$K_4 = \frac{[*COH_2][*]}{[*COH][*H]} \rightarrow [*COH_2] = K_4[*COH][*H]/[*] = K_4 K_3 K_2 [CO] K_1 [H_2][*] \quad (46)$$

$$\begin{aligned}
 K_5 &= \frac{[*\text{COH}_3][*]}{[*\text{COH}_2][*\text{H}]} \rightarrow [*\text{COH}_3] = K_5[*\text{COH}_2][*\text{H}]/[*] \\
 &= K_5 K_4 K_3 K_2 [\text{CO}] (K_1 [\text{H}_2])^{3/2} [*] \quad (47)
 \end{aligned}$$

Because the rates of steps 6 and 8 must be equal,

$$\begin{aligned}
 k_8[*\text{CH}_3][*\text{H}] &= k_6[*\text{COH}_3][*\text{H}] \rightarrow [*\text{CH}_3] = \frac{k_6[*\text{COH}_3]}{k_8} \\
 &= \frac{k_6 K_5 K_4 K_3 K_2 [\text{CO}] (K_1 [\text{H}_2])^{3/2} [*]}{k_8} \quad (48)
 \end{aligned}$$

$$K_7 = \frac{[*\text{CH}_3][*]}{[*\text{CH}_2][*\text{H}]} \rightarrow [*\text{CH}_2] = \frac{[*\text{CH}_3][*]}{K_7[*\text{H}]} = \frac{k_6 K_5 K_4 K_3 K_2 [\text{CO}] K_1 [\text{H}_2] [*]}{k_8 K_7} \quad (49)$$

The rate can be expressed as

$$\text{Rate} = k_8[*\text{CH}_3][*\text{H}] = k_6 K_5 K_4 K_3 K_2 [\text{CO}] (K_1 [\text{H}_2])^2 [*]^2 \quad (50)$$

As before,

$$1 = [*] + [*\text{H}] + [*\text{CO}] + [*\text{COH}] + [*\text{COH}_2] + [*\text{COH}_3] + [*\text{CH}_2] + [*\text{CH}_3] \quad (51)$$

Again assuming that only the coverage fractions of adsorbed CO and bare sites are appreciable, Eq. (51) reduces to

$$1 = [*] + [*\text{CO}] = [*] + K_2 [\text{CO}][*] \quad (52)$$

$$[*] = \frac{1}{1 + K_2 [\text{CO}]}$$

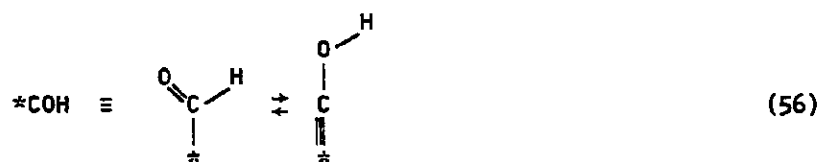
$$\text{Rate} = \frac{k_6 k_5 k_4 k_3 k_2 [\text{CO}] (K_1 [\text{H}_2])^2}{(1 + K_2 [\text{CO}])^2} \quad (53)$$

That appreciable coverages of adsorbed carbon monoxide might be expected under our reaction conditions is indicated by reports on carbon monoxide adsorption and desorption. An adsorption study on Ru (10 $\bar{1}0$) reports that carbon monoxide desorbs at 513 K (35). A study on Re (0001) reports that carbon monoxide desorbs at two different temperatures 400 K and 800 K (36). From these desorption studies, it is apparent that our assumption is good.

That no appreciable coverages of adsorbed hydrogen might be expected under our reaction conditions is indicated by reports on hydrogen adsorption and desorption. An adsorption study on Ru (0001) reports that hydrogen desorbs at 400 K (37). Another study on Ru (001) reports that hydrogen desorbs at 325 K (38). An adsorption study on polycrystalline rhenium reports that hydrogen desorbs at 450 K (39). From these desorption studies, it is apparent that our assumption that very little of the metal surface is covered with hydrogen is good.

The derivations of rate laws shown (Eqs. (42) and (53)) give the reaction orders we observed for the three catalysts investigated. Note that K_2 from these equations is the same as the K_2 's of Table 9.

Now I would like to propose structures of the surface species used in the previous derivations.





Let us consider why the mixed metal catalyst might behave differently from the single metal catalysts. The reaction temperature for the mixed metal catalyst was about the same as for the ruthenium catalyst and about 25°C lower than that used for the rhenium catalyst. I propose for the mixed metal catalyst that due to the lower reaction temperature the rhenium is essentially catalytically inactive. It serves only to dilute the active ruthenium metal.

Consider Eqs. (56), (57), (58), (61) and (62). Equation (56) has two possible structures, one with carbon triple bonded to the surface would be along the pathway of the first mechanism (Ru/Al₂O₃ and Re/Al₂O₃). The other structure, with carbon single bonded to the surface, would be along the pathway of the second mechanism (Re-Re/Al₂O₃). Assume that each bond is with a single metal atom. I propose that the triple bonded species is favored on the Ru/Al₂O₃ and Re/Al₂O₃ catalysts. This requires a three like metal atom site. The subsequent intermediates (Eqs. (57) and (58)) also require this same type of site. This type of site would not be as available on the Ru-Re/Al₂O₃ catalyst. A three ruthenium atom site would be required. The second mechanism uses single and double bonded sites which would be more available than the three center sites. Consequently, this alternate pathway is favored on the Ru-Re/Al₂O₃ catalyst.

Suggestions for Further Research

It would be interesting to continue this project to find out what effect the variation in concentrations of metals has on this reaction. Another project might be the investigation of methanation kinetics on this alloy (ruthenium and rhenium) at low pressures. Investigation of catalytic activities of other alloys would also be of interest; the alloys should have the following qualifications:

- 1) reactivity for methanation
- 2) mutual miscibility, and
- 3) similar reactivities at the same temperature.

This would create a catalyst similar to that of our study, except there would not be a diluent effect exhibited by either metal.

APPENDIX I. DERIVATION OF A RATE LAW WITH A
SIMPLE LANGMUIR-HINSHELWOOD MODEL

The following is a derivation of a rate law using Langmuir-Hinshelwood model. Two gases adsorb on a surface and react to form products.



Coverages of intermediates can be expressed by

$$K_1 = \frac{[A^*]}{[A][*]} \rightarrow [A^*] = K_1[A][*] \quad (4a)$$

$$K_2 = \frac{[B^*]}{[B][*]} \rightarrow [B^*] = K_2[B][*] \quad (5a)$$

The rate can be expressed by Eq. (3a).

$$\begin{aligned} \text{Rate [C]} &= k_3[A^*][B^*] \\ &= k_3K_1K_2[A][B][*]^2 \end{aligned} \quad (6a)$$

Expressing the number of surface site concentrations as fractional coverages, so their sum, including bare sites, is unity, we have

$$1 = [*] + [A^*] + [B^*] \quad (7a)$$

$$1 = [*] + K_1[A][*] + K_2[B][*] \quad (8a)$$

$$[*] = \frac{1}{1 + K_1[A] + K_2[B]} \quad (9a)$$

Now Eq. (6a) becomes

$$\text{Rate [C]} = \frac{K_1 K_2 k_3 [A][B]}{(1 + K_1 [A] + K_2 [B])^2} \quad (10a)$$

APPENDIX II. DERIVATION OF AVERAGE CRYSTALLITE SIZE

Starting with Eq. (17), we wish to elaborate further. Consider a simple cubic lattice with unit cell length a_0 , and assume the crystallite is a cube of side length d . Then

$$D = \frac{\text{surface atoms}}{\text{total atoms}} = \frac{6 \left(\frac{d}{a_0} \right)^2}{\left(\frac{d}{a_0} \right)^3} = \frac{6 a_0}{d} \quad (11a)$$

On solving for d , we have

$$d = \frac{6 a_0}{D} \quad (12a)$$

For a simple cubic lattice, a_0 = atom diameter; for other lattices d is similarly related to atomic diameter but the proportionality factor in Eq. (12a) differs somewhat from 6. Table 7 has been calculated from Eq. (12a) using a_0 = atomic diameter. The following data were used in calculating surface areas and crystallite size.

	Surface area of one metal atom (\AA^2) (40)	Radius of one metal atom \AA (41)
Ru	9.03	1.336
Re	9.72	1.373

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