the more rapid formation of CD<sub>4</sub> than CH<sub>4</sub> indicates that one or more of the elementary steps preceeding the rate limiting step involves the addition of hydrogen and is at equilibrium (e.g., steps 5 through 7).

The methyl groups produced in step 7 are precursors to the formation of methane and the growth of hydrocarbon chains. The former process occurs by the addition of a hydrogen atom to the methyl group and the latter by the insertion of a methylene group into the metalcarbon bond of the methyl group. Once started, chain growth can continue by further addition of methylene units to the alkyl intermediates. Termination of chain growth is postulated to occur via one of two processes - hydrogen addition to form normal alkanes and  $\beta$ -elimination of hydrogen to form  $\alpha$ -olefins. Thus, one may visualize the formation of  $C_{2+}$  hydrocarbons as a polymerization process in which methylene groups act as the monomer and the alkyl groups are the active centers for chain growth.

The proposed mechanism of methanation and chain growth is strongly supported by the results of several recent studies. Brady and Petit (14) have demonstrated that hydrocarbons can be formed by the decomposition of diazomethane over supported Ru, as well as other Group VIII metals. In the absence of  $H_2$ , ethylene is the only product observed. When  $H_2$  is added to the flow of  $CH_2N_2$ , a product distribution resembling that observed during CO hydrogenation is obtained. The authors propose that methylene groups produced by the decomposition of  $CH_2N_2$  react in the absence of adsorbed hydrogen to form ethylene. In the presence of adsorbed hydrogen, methyl groups are formed. The addition of methylene units to these species initiates chain growth. Direct evidence

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. با for the presence of methylene and  $C_1$  through  $C_4$  alkyl groups on the surface of Ru have recently been obtained using the technique of reactive scavenging (15,16). In these studies a small amount of cyclohexene is added to the synthesis gas. The products are observed to contain norcorane; methylcyclohexene; and methyl-, ethyl-, propyl-, and butylcyclohexane in addition to the usual spectrum of hydrocarbons obtained by CO hydrogenation. The appearance of products derived from cyclohexene is explained by the reaction of cyclohexene with methylene and alkyl groups, formed on the catalyst surface from CO and  $H_2$ .

Rate expressions describing the kinetics of forming methane and higher molecular weight hydrocarbons can be derived on the basis of the mechanism shown in Fig. 6, following the introduction of a number of simplifying assumptions. To begin with, it is assumed that the rate of methane formation is controlled by step 8 and that the steps preceeding it are at equilibrium. This assumption is supported by the observation of a significant inverse  $H_2/D_2$  isotope effect on the rate of methane formation over a  $Ru/Al_2O_3$  catalyst identical to that used in the present studies (13). Next, it is assumed that steps 9, 10, and 11 are irreversible and that the rate coefficients for these steps are independent of the chain length. n. The validity or this assumption will be discussed following the derivation of rate expressions for  $C_{2^+}$ hydrocarbons. Finally, it will be assumed that the fraction of vacant surface sites can be expressed as

$$\theta_{v} = \frac{1}{K_{1}P_{CO}}$$
 (1)

where K<sub>1</sub> is the equilibrium constant for reaction 1. Equation 1 is based on the infrared observations reported by Kellner and Bell (20) which show that under reaction conditions the Ru surface sites active in hydrocarbon synthesis are virtually saturated by linearly adsorbed CO and that the surface coverage by this species can be represented by a Langmuir isotherm which only involves the partial pressure of CO. The turnover number for methane formation, N<sub>C</sub>, can be written as

$${}^{N}C_{1} = {}^{k}8^{\theta}CH_{3}^{\theta}H , \qquad (2)$$

where  $k_8$  is the rate coefficient for step 8 in Fig. 6,  $\theta_{CH3}$  is the fractional coverage of the Ru surface by  $CH_3$  groups, and  $\theta_H$  is the fractional coverage by H atoms. Since equilibrium has been assumed for steps 1 through 3 and 5 through 7,  $\theta_{CH3}$  can be expressed as

$$\theta_{CH_3} = \kappa_{K}^{1.5} \kappa_{K} \kappa_{P}^{1.5} \theta_{V} / \theta_{0}$$
(3)

where  $K_i$  is the equilibrium constant for the i-th reaction and  $\theta_0$  is the fractional coverage of the Ru surface by O atoms. The magnitude of  $\theta_H$  is given by

$$\theta_{\rm H} = \kappa_{\rm 3 H}^{1/2} {}^{1/2}_{\rm P} \theta_{\rm V}$$
(4)

Substitution of eqn. 3 and 4 into eqn. 2 and introduction of eqn. 1 for results in

 $N_{C_{1}} = k_{8} \frac{K_{2}K_{3}^{2}K_{5}K_{6}K_{7}}{K_{1}^{2} \theta_{0}} \frac{P_{H_{2}}^{2}}{P_{CO}^{2}}$ (5)

The dependence of  $\mathbb{N}_{C_1}$  on  $\theta_0$  can be eliminated from eqn. 5 if it is assumed that all of the carbon and oxygen released in step 2, which does not recombine to form adsorbed CO, reacts to form hydrocarbons and water. This implies that

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$$N_{H_20} = \sum_{n=1}^{\infty} n N_{C_n}$$

where

$${}^{\rm h}{}_{\rm H_20} = \kappa_4 \theta_0 {}^{\rm p}{}_{\rm H_2} \tag{7}$$

(6)

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Since all hydrocarbon products containing two or more carbon atoms must be formed by chair growth, step 9, the overall rate of carbon consumption for the formation of hydrocarbon products can be expressed as

$$\sum_{n=1}^{n} \kappa_{C_{n}} = \kappa_{8} \theta_{CH_{3}} \theta_{H} + \sum_{n=1}^{n} \kappa_{p} \theta_{CH_{2}} \theta_{n}$$
(8)

where k is the rate constant for chain growth, step 9;  $\theta_{CH_2}$  is the fractional coverage of the Ru surface by methylene groups; and  $\theta_n$  is the fractional coverage of the Ru surface by alkyl groups of chain length n. Combining eqns. 6, 7, and 8 results in eqn. 9.

$$k_{4}\theta_{0}P_{H_{2}} = k_{8}\theta_{CH_{3}}\theta_{H} + \sum_{n=1}^{\infty} k_{p}\theta_{CH_{2}}\theta_{n}$$
(9)

Equation 9 can be solved for  $\theta_0$  in the limits where either methane or higher molecular weight products predominate. For the first case

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 $N_{C_1} >> \sum_{n=2}^{n} nN_{C_n}$ . Substitution of the expressions for  $\theta_{CH_3}$  and  $\theta_H$  into eqn. 9 results in

$$\theta_{0} = \frac{\kappa_{3}}{\kappa_{1}} \left(\frac{\kappa_{8}}{\kappa_{4}} \times \sum_{2}^{K} \sum_{5}^{K} \kappa_{6} \times \frac{1/2}{p_{CO}}\right)^{1/2} \frac{P_{H_{2}}^{1/2}}{P_{CO}}$$
(10)

which, on substitution into eqn. 5, gives

$$N_{c_1} = k_e \frac{P_{H_2}^{1.5}}{\frac{P_{CO}}{P_{CO}}}$$

11)

(12)

where

This result is identical to that obtained by Ekerdt and Bell (12). For the second case, it is assumed that

 $k_{e} = \frac{K_{3}}{K_{1}} (k_{8} k_{4} K_{2} K_{5} K_{6} K_{7})$ 

 $N_{C_1} < \sum_{n=2}^{\infty} N_{C_n}$ 

so that the first term on the right-hand side of eqn. 9 can be neglected. To solve for  $\theta_0$  in this case requires the development of expressions for  $\theta_{CH_2}$  and  $\theta_n$ . An expression for  $\theta_{CH_2}$  can be derived from the equilibrium relationships existing between steps 1,2,3,5 and 6. Thus

$$\theta_{CH_2} = \frac{K_2 K_3 K_5 K_6}{K_1 \theta_0} \frac{P_{H_2}}{P_{CO}}$$
(13)

An expression for  $\hat{\sigma}_n$  can be obtained by imposing a steady-state balance on the formation of alkyl groups containing n carbon atoms.

where  $k_{to}$  and  $k_{tp}$  are the rate coefficients for the formation of olefins and paraffins, steps 10 and 11 in Fig. 6. Solving for  $\theta_n$  results in  $\theta_n = \frac{k_p \theta_{CH_2} \tilde{e}_{n-1}}{k_p \theta_{CH_2} + k_t p \theta_H + k_t \sigma \theta_V}$  (15) Equation 15 can be rewritten in terms of the probability of chain propagation,  $\alpha$ , as

$$\theta_n = \alpha^{\dot{n}-1} \theta_{CH_3}$$
 (15)

Comparing eqns. 15 and 16 shows that

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$$\alpha = \frac{k_{p}^{\theta} CH_{2}}{k_{p}^{\theta} CH_{2} + k_{to}^{\theta} v + k_{tp}^{\theta} H}$$
(17)

The sum  $\sum_{n=1}^{\infty} e_n$ , appearing in eqn. 9, can now be expressed in closed form as

$$\sum_{n=1}^{\infty} \theta_n = \frac{\theta_1}{(1-\alpha)}$$
(18)

If  $\alpha$  is taken to be independent of  $P_{H_{2}}$  and  $P_{CO}$ , an assumption that is not rigorously correct but does not lead to significant error, then an expression for  $\theta_{0}$  can be obtained by substitution of eqns. 13 and 18 into eqn. 9. Thus,

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 $0 = k_{p}^{\theta} n - 1^{\theta} CH_{2} - k_{p}^{\theta} n^{\theta} CH_{2} - k_{tp}^{\theta} n^{\theta} H - k_{to}^{\theta} n^{\theta} V$ 

 $\theta_{0} = \left[ \frac{k_{p} K_{2}^{2} K_{3}^{2} \cdot 5 K_{5}^{2} K_{6}^{2} K_{7}}{k_{4} K_{1}^{2} (1-\alpha)} \right] \begin{array}{c} 0.33 \quad P_{H_{2}}^{0.5} \\ \frac{H_{2}}{P_{C0}^{0.67}} \end{array}$ (19)

Finally, substitution of eqn. 19 into eqn. 5 results in

$$N_{C_1} = k_e P_{H_2}^{1.5} / P_{C0}^{1.33}$$
(20)

where

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$$k_{e} = k_{8} \left[ \frac{k_{4} K_{2} K_{3}^{2} \cdot 5 K_{5} K_{6} K_{7}^{2} (1-\alpha)}{k_{p} K_{1}^{4}} \right]$$
(21)

Table III presents a comparison between the predicted dependencies of  $N_{C_1}$  on the partial pressures of  $H_2$  and CO and the dependencies determined from experimental data. It is apparent that the  $H_2$  dependence contained in both limiting forms of the expression derived for  $N_{C_1}$  is in excellent agreement with that observed in this study, as well as others. The first of the two limiting forms for  $N_{C_1}$  also provides an accurate description of the CO dependence determined from the data taken in this study. It should be noted however that while Dalla Betta and Shelef (23) have also noted an inverse first order CO dependence, other investigators (12,24) have found that the inverse dependence is less than first order.

Table III also presents a comparison between the apparent activation energies and preexponential fact ... for methane formation determined from the present results and those reported by previous

Table III. Comparison of the Rate Expressions for Methane Synthesis Obtained from Experimental Data with Those Obtained Theoretically.

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	Theory			Experiment				
		Eqn. 11	Eqn. 20, ;	This 	Dalla Betta et al. (23)	Vannice (24)	Ekerdt and Bell (12)	
Catal	yst			1% Ru/A1203	1.5% Ru/Al203	5% Ru/A1203	5% Ru/SiO2	
A atm	(m-n) <sub>s</sub> -	1 _	-	$1.3 \times 10^9$	3.2 x 10 <sup>7</sup>	5.6 x 10 <sup>8</sup>	$2.2 \times 10^9$	
E <sub>a</sub> (kc	al/mole	) -	-	28.2	24	24.2	24.1	
;	m	1.5	1.5	1.35	1.8	1.6	1.5 .	
	n	-1.0	-1.33	-0.99	-1.1	-0.6	-0.6	

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investigators. It is seen that the activation energy determined in this study is about 4 kcal/mole higher than that reported earlier. At present there is no explanation for this difference. A substantial variation is observed in the values of the preexponential factors reported by different authors. It is conceivable that a major part of these differences may be related to the precision used in measuring the Ru dispersion and to the effects of dispersion on catalyst activity. As noted by King (25), and Kellner and Bell (26), the specific activity of Ru decreases as the dispersion of the metal increases.

Expressions describing the rates of formation of higher molecular weight products can be derived in a manner similar to that followed in developing an expression for the rate of methane formation. The turnover frequencies for the formation of normal paraffins and  $\alpha$ -clefins can be expressed as follows:

$$N_{C_{n}} = k_{tp} \theta_{H} \theta_{n}$$
 (22)

$$N_{C_n} = k_{to} \theta_v \theta_n$$
 (23)

Summing eqns. 22 and 23 to obtain an expression for the rate of formation of products containing n carbon atoms and substituting from eqn. 16 for  $\theta_n$  results in

$$N_{C_n} = (k_{to}\theta_v + k_{tp}\theta_H)\alpha^{n-1}\theta_{CH_3}$$
(24)

Substitution of  $\theta_{CH_3}$  by  $N_{C_1}/(k_8\theta_H)$  and substitution from eqns. 1 and 4 for  $\theta_v$  and  $\theta_H$  leads to

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$$= (1 + \beta / P_{H_2}^{0.5}) \alpha^{n-1} N_{C_1}, \qquad (25)$$

assuming that  $k_{tp} = k_8$ . The parameter  $\beta$  appearing in eqn. 25 is defined as

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$$k = \frac{k_{to}}{k_{tp} \kappa_3^{1/2}}$$
 (26)

and is related to the ratio of olefin to paraffin formation in the following fashion:

$$\frac{N_{C_{n}}}{N_{C_{n}}} = \beta/P_{H_{2}}^{0.5}$$
(27)

The form of eqn. 25 suggests that a plot of log  $(N_{C_n}/N_{C_1})$  versus (n-1) should be a straight line with a slope given by log  $\alpha$ . The results presented in Figs. 2 and 3 were plotted in this fashion. As was noted earlier, with the exception of the point for n = 2, the data taken at 1 atm are in good agreement with eqn. 25. At 10 atm, eqn. 25 also provides a good description of the data, with the exception of the points at n = 2 and 3. A more complete discussion of the slope of the lines shown in Figs. 2 and 3, and its dependence on reaction conditions, will be presented below.

It is of interest at this point to consider whether the kinetics represented by eqn. 25 are consistent with the type of product distribution described by Friedel and Anderson (27) and Henrici-Olive and Olive (28). According to these authors the fraction of the total carbon converted to hydrocarbons which contain n carbon atoms,  $f_n$ , should be given by

$$f_n = n\alpha^{n-1}(1-\alpha)^2$$
 (28)

and, consequently, a plot of  $\log(f_n/n)$  versus n should be a straight line of slope  $\alpha_n$  and intercept  $\log (1-\alpha)^2/\alpha$ . The derivation of eqn. 28, which is often referred to as a Schultz-Flory distribution in the recent literature on Fischer-Tropsch synthesis (28-34), is based on the assumption that chain growth occurs by the addition of single carbon intermediates and that chain termination leads to the formation of stable products. No regard need be given in this derivation to the details of the chain propagation or termination steps.

The expressions contained in eqn. 25 for the kinetics of olefin and paraffin synthesis are consistent with a Schulz-Flory distribution, provided one considers products of a homologous series, viz. only olefins or paraffins. This statement can be verified by starting out with the defining equations for the fraction of products within a homologous series, which contain a given number of carbon atoms.

$$f_{n} = \frac{{}^{nN}c_{n}}{\sum_{n=1}^{\infty} {}^{nN}c_{n}}$$
(29)

$$f_{n}^{=} = \frac{\frac{nN_{c}}{n}}{\sum_{n=2}^{\infty} \frac{nN_{c}}{n}}$$
(30)

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Notice that the surmation for paraffins runs from one to infinity while that for olefins runs from two to infinity. Substitution of the first and second terms of eqn. 25 into eqns. 29 and 30, respectively, gives

$$\hat{r}_{n} = n\alpha^{(n-1)}(1-\alpha)^{2}$$
 (31)

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$$f_{\alpha}^{=} = \frac{n\alpha^{(n-1)}(1-\alpha)^{2}}{1-(1-\alpha)^{2}}$$
 (32)

Equation 31 and the numerator of eqn. 32 are identical to eqn. 28. The denominator appearing in eqn. 32 arises from the fact that the summation in eqn. 30 begins with n = 2.

Figures 7 and 8 illustrate plots of  $f_n^-/n$  and  $f_n^-/n$  versus (n-1) for data obtained at 1 and 10 atm. Both figures show that, with the exception of the point at n = 2, the experimental values of  $f_n^-/n$  fall along a straight line. The slope of the line is equal to log  $\alpha$ , and, as can be seen in Table IV, the values of  $\alpha$  determined from Figs. 7 and 8 are very close to those determined from plots of  $N_{C_n}/N_{C_1}$ . Equation 30 can be tested further by comparing the intercept of the line passed through experimental values of  $f_n^-/n$  with the expression  $(1-\alpha)^2/[1-(1-\alpha)^2]$  obtained from eqn. 30 for (n-1) = 0. Table IV indicates that the intercepts evaluated from Figs. 7 and 8 are somewhat larger than those predicted by eqn. 30. This difference can be explained if it is assumed that the low value of  $f_2^-/2$  is due to a partial conversion of ethylene to ethane. Under this circumstance the difference between  $2\alpha(1-\alpha)^2/[1-(1-\alpha)^2]$  and the experimentally observed value of  $f_2^-$  would correspond to the carbon number fraction of the



Fig. 7. Plots of  $f_n^{=}/n$  and  $f_n^{-}/n$  versus (n-1) for P = 1 atm.



Fig. 8. Plots of  $f_n^{=}/n$  and  $f_n^{-}/n$  versus (n-1) for P = 10 atm.

	$\mathbf{P} = 1 \mathbf{z}$	atm <sup>a</sup>	$P = 10 atm^{a}$		
	Source	Value	Source	Value	
<u>-</u> , х	Fig. 7	0.62	Fig. 8	0.61	
ደ ኬ	Fig. 2	0.66	Fig. 3	0.63	
£	: . Fig. 7	0.20	Fig. 8	0.23	
f <sub>1</sub>	$(1-\alpha)^2$	0.18	$(1-\alpha)^2$	0.17	
-	1-(1-c.) <sup>2</sup>		$[1-(1-\alpha)^2]$		
f	See note c	0.21	See note c	0.21	
$f_1$	Fig. 7	0.66	Fig. 8	0.44	
È_1	$(1-\alpha)^2$	0.14	$(1-\alpha)^2$	0.18	
f	See note d	0.64	See note d	0.41	

Table IV. Comparison of the Observed Product Distributions with Schultz-Flory Distributions for Olefins and Paraffins.

 $f_{1}^{=} = \frac{(1-\alpha)^{2}/[1-(1-\alpha)^{2}]}{1-2\left\{(1-\alpha)^{2}/(1-(1-\alpha)^{2}-f_{2}^{2}/2\right\}\right\}}$ 

<sup>b</sup>Intercept at (n-1) = 0

<sup>d</sup> 
$$f_1^- = (1-\alpha)^2 + \sum_{n=2}^{\infty} n \left[ \alpha^{(n-1)} (1-\alpha)^2 - f_n/n \right]$$

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ethylene converted to ethane. Imposing this correction leads to predicted intercepts which are in much closer agreement with those from the experimental results.

Equation 31 predicts that the values of  $f_n/n$  should also lie along a straight line on a plot of log  $(f_n/n)$  versus (n-1). Figure 7 shows that at 1 atm the point for methane lies well above the line given by eqn. 31, the points for n = 2 through 8 fall below the line, and only the points for n = 9 and 10 lie near the line. The agreement between theory and experiment is somewhat better at 10 atm. In this case Fig. 8 shows that the point for methane lies above the line, the points for n = 2 and 3 lie below the line, but the points for n = 4 through 8 lie along the line. The remaining two points, for n = 9 and 10, lie slightly above the line. The pattern of the deviations between theory and experiment observed in Figs. 7 and 8 suggests that a part of the C<sub>2+</sub> paraffinic product undergoes hydrogenolysis to form methane. Based on this interpretation, the correct value of  $f_n$  should be given by

$$f_{1}^{-} = (1-)^{2} + \sum_{n=Z}^{\infty} n \left[ \alpha^{(n-1)} (1-\alpha)^{2} - f_{n}^{-} / n \right]$$
(33)

Values of  $f_1^-$  determined in this fashion are listed in Table IV and are seen to be in good agreement with the values of  $f_1^-$  observed experimentally. The fact that the formation of excess methane is lower at higher pressure is consistent with the proposed interpretation. For the same H<sub>2</sub>/CO ratio, elevation of the total pressure causes a reduction in  $\theta_v$ , due to the higher CO partial pressure, and, hence, a

reduction in the availability of sites for paraffin adsorption. The decline in the extent of paraffin hydrogenolysis with increasing carbon number might be ascribed to the fact that with increasing molecular weight a higher number of contiguous vacant sites might be required for initial adsorption. Finally, it should be noted that in addition to explaining the discrepancies in the distribution of paraffins presented in Figs. 7 and 8, the occurrence of hydrogenolysis would explain why in Figs. 2 and 3 the experimental points for n = 2 and 3 fall below a straight line passed through the balance of the data.

The form of eqn. 27 indicates that plots of  $N_{C_{\pi}^{=}/N_{C_{\pi}^{=}}}$  versus  $P_{H_{2}}^{-0.5}$ should result in straight lines with a slope of  $\beta$  which is independent of n. Figure 9 illustrates a test of this prediction for n = 2, 3,and 4. The data plotted in this figure were taken at pressures between 1 and 10 atm and  $H_2/CO$  ratios between 1 and 3, and at temperatures of 498K to minimize the effects of olefin hydrogenation. For each value of n the data are seen to scatter around a straight line, in general agreement with eqn. 27 and consistent with the empirical rate expressions presented in Table I. It is apparent, though, that the slopes of the lines are dependent on the value of n. This dependence is seen even more clearly in Fig. 10 which shows a plot of  $\beta$  versus n for n = 2 through 10. In light of the discussion presented in connection with Figs. 7 and 8, it seems reasonable to propose that the high values of  $\beta$  for n = 2 and 3 may be due, in part, to a partial hydrogenolysis of ethane and propane. The balance of the variation in  $\beta$  with n may be due to a dependence of the rate coefficients for chain termination on



Fig. 9. Plots of  $N_{C_n} = N_{C_n}$  versus  $P_{H_2}^{-0.5}$ .



Fig. 10. Plot of  $\beta$  versus n.

the value of n. A more detailed interpretation of these observations is not possible at present and must await further study.

The temperature dependence of  $N_{C_n}^{=/N} c_n^{-}$ , which was shown in Fig. 4, can be interpreted in terms of the rate and equilibrium constants appearing in the definition of  $\beta$ , eqn. 26. The difference in the apparent activation energies for the formation of olefins and paraffins,  $E_{op}$ , are related to the activation energies for the reactions of alkyl species to form olefins and paraffins.  $E_o$  and  $E_p$ , and to the heat of  $H_2$  adsorption,  $\Delta H_{H_2}$ , by the following expression

$$E_{op} = E_{o} - E_{p} - \frac{H_{H_2}}{H_2}$$
 (34)

Assuming that  $\Delta H_{H_2}$  is about -20 kcal/mole, a value typical for group VIII metals (35), leads to the conclusion that  $(E_p - E_o) \approx 4$  kcal/mole.

A relationship for the dependence of  $\alpha$ , the probability of chain growth, on the partial pressures of H<sub>2</sub> and CO can be determined starting from the definition for  $\alpha$ , 2qn. 17. Substitution of eqns. 1, 4, 13, and 19 for  $\vartheta_v$ ,  $\vartheta_H$ ,  $\vartheta_{CH_2}$ , and  $\vartheta_0$  (assuming that  $N_{C_1} \ll \sum_{n=2}^{\infty} nN_{C_n}$ ) gives the following expression:

$$\alpha = \left[1 + \nu(1-\alpha)^{-0.33} - 0.67 - 0.67 - 0.5 \right]^{-1}$$
(35)

where

$$v = \left[\frac{K_3}{k_p^2 k_4 K_1^2 K_2 K_5 K_6}\right] 0.33$$
(36)

Rearrangement of eqn. 36 provides a more explicit equation for  $\alpha$ , which can be solved by means of trial and error.

$$\alpha^{-1}(1-\alpha)^{1.33} = \bigvee_{\substack{P \\ CO}} P^{-0.67}(1 + \beta P^{-0.5})$$
(37)

The utility of eqn. 37 as a representation for the dependence of  $\alpha$  on the partial pressures of H<sub>2</sub> and CO, and on the temperature can now be examined. To do so requires that values of  $\beta$  and  $\nu$  be determined first. An expression for  $\beta$  can be obtained from the data presented in Figs. 4 and 10. Choosing the value of  $\beta$  for n = 4 as being representative leads to the following equation:

$$\beta = 1.8 \times 10^3 \exp(-5,700/RT)$$
 (38)

An equation for v can be obtained by forcing an agreement between eqn. 37 and the values of v determined at I atm for  $H_2/CO = 2$  and temperatures of 498, 523, and 543K. The resulting expression is given by

 $v = 1.2 \exp(-4,100/RT)$  (39)

A comparison between the experimental and predicted values of  $\alpha$  is presented in Table V. It is observed that at 1 atm, eqn. 37 provides an accurate representation of the dependence of  $\alpha$  on temperature as well as H<sub>2</sub> and CO partial pressures. When the total pressure is increased to 10 atm, eqn. 37 predicts values of  $\alpha$  which are substantially higher than those observed experimentally. Nevertheless, the

•	values of $\alpha$ .			
P(atm)	т(к)	н <sub>2</sub> /со	α Pradicted	ب Experimental
1	548 <sup>°</sup>	1.	0.55	0.56
		2	0.52	0.51
		3	0.49	0.47
1	523	1 :	0.63	0.62
		2	0.60	0.61
		3.	0.57	0.60
1	498	1	0.71	0.69
		<b>2</b> :	0.68	0.68
		3	0.66	0.66
10	548	1	0.90	0.61
	•	2 .	0.89	0.60
		3	0.88	0.58
10	523	3	. 0.91	0.61
10	498	1,	0.94	0.67
	, ,	2	0.94	0.63
	·	·. 3	0.93	0.63

Table V. Comparison of Predicted and Experimentally Observed Values of a. reduced dependence of  $\alpha$  on  $\text{H}_2$  and CO partial pressures observed at 10 atm is properly reflected.

The failure of eqn. 37 to provide an accurate estimation of  $\alpha$  at 10 atm is not well understood. A possible explanation might be that at higher pressures additional termination steps become important. Inspection of eqn. 17 shows that this would cause a decrease in  $\alpha$ . A reaction which might contribute to such an effect would be the insertion of GO into the metal-carbon bond of an alkyl group to form an acyl species which might subsequently react to produce either an aldehyde or an alcohol. Alternatively, one might consider the reaction of surface methylene or alkyl groups with olefins present in the reaction products (15,16). The results presented in Fig. 5 show that under the reaction conditions used in the present work, ethylene does not participate extensively in this type of reaction. However, this does not exclude the possibility that higher molecular weight olefins might be more reactive than ethylene. As a consequence further investigation will be needed to establish the effects of additional chain termination reactions and secondary reactions on the magnitude of  $\alpha$ .

#### CONCLUSIONS

In the present paper it has been shown that the reaction mechanism presented in Fig. 6 explains many aspects of CO hydrogenation over Ru. Rate expressions derived from this mechanism accurately describe the kinetics for the synthesis of methane and higher molecular weight hydrocarbons. It has been shown that  $C_{2+}$  olefins and paraffins are formed from a common precursor, and that, in the absence of further olefin hydrogenation, the olefin to paraffin ratio in the products depends only on the H, partial pressure. It has also been demonstrated that the products in a homologous series follow a Schultz-Flory distribution. Minor deviations from such a distribution observed for olefins can be ascribed to a partial conversion of ethylene to ethane. The much more significant deviations found for paraffins appears to be due to a partial hydrogenolysis of C2+ alkanes, a process which seems to predominate at low CO partial pressures. Finally, it is concluded that the proposed mechanism can be used to deduce an expression for the effects cf reaction conditions on the probability of chain growth, α. This expression provides an excellent correlation of the experimental results obtained at 1 atm but overpredicts the values of  $\alpha$  observed at 10 atm. It is hypothesized that the discrepancy observed at higher pressures may indicate the presence of chain termination processes not included in the preposed mechanism.

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# CHAPTER V

Synthesis of Oxygenated Products from Carbon Monoxide and Hydrogen Over Silica- and Alumina-Supported Ruthenium Catalysts

### ABSTRACT

The synthesis of oxygenated products over supported ruthenium catalysts was investigated using both  $H_2/CO$  and  $D_2/CO$  feed mixtures. Acetaldehyde was the principal oxygenated product formed over silicasupported ruthenium. By contrast, methanol was the principal oxygenated species formed over an alumina-supported catalyst. A significant inverse  $H_2/D_2$  isotope effect was observed on the rate of formation of both acetaldehyde and methanol. The kinetics of acetaldehyde synthesis were determined and compared with those for methane synthesis. The form of the rate expressions obtained for each product and the origins of the observed isotope effects are explained in terms of a mechanism for the synthesis of both products. A reaction mechanism for methanol synthesis is also proposed.

#### INTRODUCTION

It is well recognized that oxygenated products such as alcohols, aldehydes, acids, etc. are produced in parallel with hydrocarbons during Fischer-Tropsch synthesis over iron and cobalt catalysts (1). By contrast, though, very little is known about the synthesis of oxygenated compounds over ruthenium. The purpose of the present investigation was to establish the activity of  $\operatorname{Ru}/\operatorname{SiO}_2$  and  $\operatorname{Ru}/\operatorname{Al}_2\operatorname{O}_3$  catalysts for the synthesis of such compounds and to shed some light on the mechanisms by which these products are formed. For this purpose rate data were acquired, over a broad range of reaction conditions, using both  $\operatorname{H}_2/\operatorname{CO}$  and  $\operatorname{D}_2/\operatorname{CO}$  feed mixtures.

#### EXPERIMENTAL

Preparation of the 1.2% Ru/SiO, and 1.0% Ru/A1,03 catalysts used in this study have been described in detail elsewhere (2,3). The initial dispersion of the alumina-supported catalyst determined by H2 chemisorption, was found to be near unity. Measurements of dispersion following use of this catalyst showed that the dispersion gradually decreased to about 0.6 and remained fairly constant thereafter. The dispersion of the silica-supported catalyst could not be determined by H, chemisorption since the uptake of H, even at elevated temperatures, was exceedingly slow, and hence the point at which equilibrium was attained could not be established reliably. As a result, the dispersion of this catalyst was measured by CO chemisorption and determined to be 0.25, based on the assumption that the ratio of CO to surface Ru atoms is unity. The valudity of this assumption is supported by previous studies with low dispersion Ru/Al<sub>2</sub>O<sub>3</sub> catalysts (5) and by

the observation that infrared spectra of CO adsorbed on the  $Ru/SiO_2$ used in this study (6) show only a single band, attributable to linearly adsorbed CO.

The experimental apparatus and procedure have been described previously (2). All of the experiments were carried out in a stainless steel microreactor heated in a fluidized bed. A premixed feed composed of  $H_2(D_2)$  and CC at a ratio of  $H_2(D_2)/CO = 3.0$  was supplied to the reactor and the product gas was analyzed by a gas chromatograph equipped with flame ionization detectors. The detector sensitivities for deuterated and hydrogenated products were established to be identical by injecting pure samples of  $CH_4$  and  $CD_4$ .

Each experiment with a fresh catalyst charge (100 mg) was initiated by a 10 to 12 hr reduction in flowing  $H_2$  at 673K and 10 atm. The temperature was then lowered to 498K and the feed mixture was introduced at a flow rate of 200 cm<sup>3</sup>/min (NTP). Ten minutes after the reaction began, a gas sample was taken for analysis and the gas feed was switched over to pure  $H_2$  for 1 hr. By alternating short reaction periods and longer reduction periods, a stable catalyst activity could be achieved after several cycles. Once this status was attained, the catalyst was cooled to 453K and data were taken between 453 and 498K. The catalyst was then heated to 548K, and data were taken between 548 and 498K. By following this procedure, a check could be obtained for catalyst deactivation. In all cases the reaction rate measured at 498K could be reproduced to within a few percent. It should be noted further, that in all instances the conversion of CO was low, ranging from 0.02% at 453K to 1.5% at 548K.

### RESULTS

### Ru/SiO,

The primary oxygen-containing organic product produced over the  $Ru/SiO_2$  catalyst was acetaldehyde. Measurements of the rate of formation of this product as well as the rate of methane formation were obtained at pressures of 1 and 10 atm, over the temperature range of 448 to 548K, using H<sub>2</sub>/CO ratios of 1 and 3. The kinetics for producing both products could be represented by power law expressions, and the constants appearing in these relations were determined by means of a nonlinear least-squares regression analysis. The resulting expression for acetaldehyde is given by

$$N_{CH_3CHO} = 7.1 \times 10^2 P_{H_2}^{0.6} \exp(-15,000/RT)$$
 (1)

and that for methane by

$$N_{CH_4} = 8.0 \times 10^9 P_{H_2}^{1.3} P_{CO}^{-1.0} \exp(-29,000/RT).$$
 (2)

In both equations, the rates of acetaldehyde and methane synthesis,  $N_{CH_3CHO}$  and  $N_{CH_4}$ , are expressed in molecules of product produced per second per Ru surface site, and the partial pressures of H<sub>2</sub> and CO,  $P_{H_2}$  and  $P_{CO}$ , are expressed in atmospheres. Deviations of less than  $\pm$  7% were observed between the rates predicted by eqns. 1 and 2 and the rates of each product observed experimentally. It is of further interest to note that eqn. 2 is in very good agreement with the rate

expression recently reported for methane synthesis over the  $Ru/Al_2O_3$  catalyst used in the present studies (4).

Substitution of  $D_2$  for  $H_2$  in the synthesis gas mixture affects the rates of acetaldehyde and methane formation. Figure 1a shows Arrhenius plots for the formation of acetaldehyde from  $H_2/CO$  and  $D_2/CO$ mixtures at 1 and 10 atm. At both pressures the rate of acetaldehyde formation is seen to be approximately twice as rapid when  $D_2$  rather than  $H_2$  is present in the feed. Figure 1b shows that the rate of methane formation is influenced to a much lesser degree when  $D_2$  is substituted for  $H_2$ . At 10 atm, the rate of CD<sub>4</sub> formation is approximately 1.1 times that observed for CH<sub>4</sub>; however, no isotope effect can be observed at 1 atm.

# <u>Ru/A1,03</u>

In contrast to the  $Ru/SiO_2$  catalyst, the  $Ru/Al_2O_3$  catalyst was active for the formation of methanol but produced very little acetaldehyde. For a given temperature, pressure, and  $H_2/CO$  ratio, the rate of methanol formation was found to be a strong function of the feed flow rate. As shown in Fig. 2, the observed rate of methanol formation increases substantially with increasing flow rate and coproaches a plateau at high flow rates. Since the rate of forming methane and  $C_{2+}$  hydrocarbons is unaffected by flow rate, the trend observed in Fig. 2 suggests that at low flow rates, a part of the methanol formates (7). The duration of each experiment also has a strong influence on the production of methanol. Figure 3 shows that the rate of methanol



Fig. 1. Arrhenius plots for the synthesis of acetaldehyde and methane from  $\mathrm{H}_2(\mathrm{D}_2)$  and CO over a silica-supported Ru catalyst.



Fig. 2. Effect of feed flow rate on the rate of methanol synthesis over an alumina-supported Ru catalyst.

synthesis increases from practically zero to an asymptotic level, over a 20 min period. During the same interval, the rate of methane formation declines by about a third. While not shown, a similar decline was also observed in the formation of  $C_{2+}$  products. The similarities in the dynamics of the deactivation of the catalyst for hydrocarbon synthesis and its apparent activation for methanol synthesis suggest that the latter trend is due to a progressive poisoning or deactivation of the catalyst sites responsible for methanol decomposition.

The influence of total pressure and  $H_2/CO$  ratio on the synthesis of methane and methanol is presented in Table I. As can be seen, both rates increase with increasing pressure and  $H_2/CO$  ratio. The formation of methanol relative to methane is favored at high pressures, but the  $H_2/CO$  ratio has only a negligible influence on the product selectivity ratio. The effects of temperature on the rates of methanol and methane synthesis are shown in Fig. 4. The apparent activation energies for methanol and methane synthesis determined from these data are 21.6 and 28 kcal/mole, respectively. Arrhenius plots for the synthesis of methanol and methane from  $D_2$  and CO are also shown in Fig. 4. Utilization of  $D_2$  in the feed gas increases the absolute rate of methanol synthesis by a factor of 1.6 over that observed for a feed containing  $H_2$ and CO and increases the rate of methane formation by a factor of 1.4.



synthesis over an alumina-supported Ru catalyst.

	l.	
(Atm)	N <sub>CH3OH</sub> (s <sup>-1</sup> )	N <sub>CH4</sub> (s <sup>-1</sup> )
10	$1.5 \times 10^{-3}$	$2.5 \times 10^{-3}$
5	$9.7 \times 10^{-4}$	$2.0 \times 10^{-3}$
1	$2.4 \times 10^{-4}$	$1.3 \times 10^{-3}$
10	$9.7 \times 10^{-4}$	$1.4 \times 10^{-3}$
5	$7.0 \times 10^{-4}$	$1.1 \times 10^{-3}$
1	$1.4 \times 10^{-4}$	$6.6 \times 10^{-4}$
10	$6.0 \times 10^{-4}$	8.7 x $16^{-4}$
5	$3.4 \times 10^{-4}$	$6.7 \times 10^{-4}$
1	$7.3 \times 10^{-5}$	$4.0 \times 10^{-4}$
	(Atm) 10 5 1 10 5 1 10 5 1 10 5 1 10 5 1 10 5 1 10 5 1 10 5 1 10 5 1 10 5 1 10 5 1 10 5 1 10 5 1 10 5 1 10 5 1 10 5 1 10 5 1 10 5 1 1 10 10 10 10 10 10 10 10	(Atm) $N_{CH_3OH}$ (s <sup>-1</sup> ) 10 1.5 x 10 <sup>-3</sup> 5 9.7 x 10 <sup>-4</sup> 1 2.4 x 10 <sup>-4</sup> 10 9.7 x 10 <sup>-4</sup> 5 7.0 x 10 <sup>-4</sup> 1 1.4 x 10 <sup>-4</sup> 10 6.0 x 10 <sup>-4</sup> 5 3.4 x 10 <sup>-4</sup> 1 7.3 x 10 <sup>-5</sup>

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Table I. The Effects of H<sub>2</sub>/CO Ratio and Pressure on the Rates of Methanol and Methane Formation Over a 1.0% Ru/Al<sub>2</sub>O<sub>3</sub> Catalyst at 498K.


#### DISCUSSION

The mechanism of acetaldehyde formation can be envisioned as an extension of the mechanism recently proposed (4,8) to explain the synthesis of hydrocarbons over Ru catalysts. Since detailed discussions of the steps entering the latter scheme have already been presented, only a brief summary will be given here. As may be seen in Fig. 5, the synthesis of hydrocarbons is initiated by dissociative chemisorption of CO and H2. Stepwise hydrogenation of the atomic carbon, released by CO dissociation, results in the formation of methyl groups. These species then act as precursors to the formation of both methane and  $C_{2+}$ olefins and paraffins. The first of these products is formed by hydrogen addition to the methyl group, while the growth of hydrocarbon chains is initiated by the addition of a methylene group. Olefins and paraffins are formed by either  $\beta$ -hydrogen elimination from, or  $\alpha$ -hydrogen addition to, the adsorbed alkyl intermediates. The formation of acetaldehyde is proposed to occur via a two step process. In the first, CO is inserted into the metal-carbon bond of a methyl group. The addition of hydrogen to the resulting acetyl group then produces acetaldehyde in the second step. It should be noted that higher molecular weight aldehydes could be formed via similar processes starting with alkyl groups containing two or more carbon atoms.

The proposed mechanism of acetaldehyde formation is supported by a number of precedents originating in the field of coordination chemistry. The insertion of CO into the metal-carbon bond of transition metal complexes, containing methyl ligands, is well documented (9,10)

1. 
$$CO + S = CO_{S}$$
  
2.  $CO_{S} + S = C_{S} + O_{S}$   
3.  $H_{2} + 2S = 2H_{S}$   
4.  $O_{S} + H_{2} \rightarrow H_{2}O + S$   
5.  $C_{S} + H_{S} = CH_{S} + S$   
6.  $CH_{S} + H_{S} = CH_{2_{S}} + S$   
7.  $CH_{2_{S}} + H_{S} = CH_{3_{S}} + S$   
8.  $CH_{3_{S}} + H_{S} \rightarrow CH_{4} + 2S$   
9.  $CH_{3_{S}} + CH_{2_{S}} \rightarrow C_{2}H_{5_{S}} + S$   
10.  $C_{2}H_{5_{S}} + S \rightarrow C_{2}H_{4} + H_{5} + S$   
11.  $C_{2}H_{5_{S}} + H_{S} \rightarrow C_{2}H_{6} + 2S$   
12.  $CH_{3_{S}} + CO_{S} \rightarrow CH_{3}CO_{S}$   
13.  $CH_{3}CO_{S} + H_{S} \rightarrow CH_{3}CHO + 2S$   
14.  $C_{2}H_{5_{S}} + CH_{2_{S}} \rightarrow C_{3}H_{7_{S}} + S$ 

etc.

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# Fig. 5. Proposed mechanism for the synthesis of hydrocarbons and acetaldehyde.

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and is believed to occur via migration of the methyl group to form an acetyl group (9). CO insertion has also been demonstrated to occur during the hydroformylation of ethylene, catalyzed by transition metal complexes (11). The formation of acetyl derivatives has been reported via the reaction of  $CH_3RuCp(CO)_2$  in the presence of tertiary phosphines. It has been noted (9,12), though, that these acetyl complexes are not as stable as those produced with metals appearing further to the left in the transition series. Acetyl derivatives can also be formed from acetaldehyde. Thus, for example (13), the reaction of  $Os(CO)_2(PPh)_3$ with excess acetaldehyde produces structure I.



In view of this result and the concept of microreversability, it seems reasonable to suggest that the formation of acetaldehyde can occur by reductive elimination of an acetyl group (step 13 in Fig. 5).

If it is assumed that reactions 8 and 12 are the rate limiting steps for the formation of methane and acetaldehyde, respectively, then the rate of formation of each product can be described by eqns. 3 and 4.

$${}^{N}CH_{4} = {}^{k}8 {}^{\theta}CH_{3} {}^{\theta}H$$
 (3)

$${}^{\mathrm{N}}\mathrm{CH}_{3}\mathrm{CHO} = {}^{\mathrm{k}}_{12} {}^{\theta}\mathrm{CH}_{3} {}^{\theta}\mathrm{CO}$$
(4)

where  $k_8$  and  $k_{12}$  are the rate coefficients for reactions 8 and 12, respectively, and  $\theta_{CH_3}$ ,  $\theta_H$ , and  $\theta_{CO}$  are the fractional coverages of the catalyst surface by adsorbed  $CH_3$  groups, H atoms, and CO, respectively. Under the assumptions that reactions 1 through 3 and 5 through 7 are at equilibrium and that atomic oxygen is removed from the catalyst surface at the same rate that methane is formed, it has previously been shown (4,8) that  $\theta_{CH_3}$ ,  $\theta_{CO}$ , and  $\theta_H$  can be represented by

$$\theta_{CH_{3}} = {\binom{k_{4}}{k_{8}}}^{1/2} {\binom{k_{2}K_{3}K_{5}K_{6}K_{7}}{K_{7}}}^{1/2} \frac{P_{H_{2}}}{C_{0}}.$$
(5)
$$\theta_{C0} = K_{1}P_{C0}\theta_{V}$$
(6)

$$\theta_{\rm H} = \kappa_{3}^{1/2} P_{\rm H}^{1/2} \theta_{\rm v}, \qquad (7)$$

where  $k_i$  is the rate coefficient for reaction i,  $K_i$  is the equilibrium constant for reaction i, and  $\theta_v$  is the fraction of the catalyst surface which is vacant. Furthermore, in situ infrared studies (6,14,15) indicate that

$$\theta_{\rm CO} \simeq 1.0$$
 (8)

and

$$\theta_{v} = \frac{1}{K_{1}P_{CO}}$$
(9)

Substitution of eqns. 5, 6, and 7 into eqns. 3 and 4, and elimination of  $\theta_{CO}$  and  $\theta_{v}$  from the resulting equations by substitution from eqns.

8 and 9, leads to the following rate expressions for methane and . . acetaldehyde:

$$N_{CH_4} = \frac{K_3}{K_1} \left( k_8 k_4 K_2 K_5 K_6 K_7 \right)^{1/2} \frac{p_{H_2}^{1.5}}{p_{CO}^{2}}$$
(10)

$$N_{CH_{3}CHO} = k_{12} \left(\frac{k_{4}}{k_{8}}\right)^{1/2} \left(K_{2}K_{3}K_{5}K_{6}K_{7}\right)^{1/2} P_{H_{2}}$$
(11)

It should be noted that eqn. 10 is identical to the expression derived in previous discussions of methane synthesis based upon the mechanism presented in Fig. 5 (4,8).

Comparizon of eqns. 2 and 10 shows that the rate expression for methane synthesis obtained theoretically is in reasonably good agreement with that observed experimentally using the Ru/SiO<sub>2</sub> catalyst. A similar level of agreement is also noted for acetaldehyde synthesis, as may be judged by comparison of eqns. 1 and 11.

The mechanism outlined in Fig. 5 also provides a basis for understanding the origin of the inverse isotope effects observed for acetaldehyde and methane synthesis and the reason why the effect is larger for acetaldehyde. To proceed, we must first examine the influence of isotopic substitution on the factors entering into eqns. 3 and 4. A normal primary kinetics isotope effect is expected for reaction 8, since this reaction involves the addition of a hydrogen atom (16). Consequently,  $k_8^H$  should be larger than  $k_8^D$ . Since hydrogen is not involved directly in reaction 12, only a secondary kinetic isotope effect is expected, and  $k_{12}^H$  should be approximately equal to  $k_{12}^D$ . The only factor influencing the fractional surface coverage by hydrogen, which is sensitive to isotopic substitution, is  $K_3$ . An analysis of the ratio  $K_3^{\rm H}/K_3^{\rm D}$  based upon statistical mechanics (2) shows that  $1.27 < K_3^{\rm H}/K_3^{\rm D} < 1.51$  for temperatures between 453 and 543K. Consequently, we can deduce from eqns. 7 and 9 that  $\theta_{\rm H} > \theta_{\rm D}$ .

Examination of eqn. 5 indicates that several factors will influence the relative magnitudes of  $\theta_{CH_3}$  and  $\theta_{CD_3}$ . The ratio of the rate coefficients for reactions 4 and 8 should contribute only a small effect since similar primary kinetic isotope effects are expected for reactions 4 and 8. Reaction 2 will not exhibit an isotope effect and the isotope effect on reaction 3 has already been discussed. An inverse equilibrium isotope effect should occur for reactions 5 through 7, since these reactions involve the addition of a hydrogen atom to a  $C_1$  intermediate in a reversible process (16). Taking all of the factors into account, and recognizing that the inverse isotope effect associated with the product  $K_5K_6K_7$  should be larger than the normal isotope effect associated with  $K_3$ , it seems reasonable to expect that  $\theta_{CD_3}$  will be larger than  $\theta_{CH_2}$ .

The isotope effects predicted for  $k_8$  and  $\theta_{CH_3}$  in the preceding discussion can be confirmed by a comparison of the overall isotope effects associated with the formation of methane and acetaldehyde. As the first step in this process, eqns. 3\_and 4 are combined to obtaineque. 12.

<sup>N</sup>CH<sub>4</sub> = 
$$\frac{k_8 K_3^{1/2}}{k_{12} K_1} \frac{\frac{P_{H_2}}{P_{CO}}}{\frac{P_{H_2}}{P_{CO}}} N_{CH_3CHO}$$
 (1)

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The matio  $N_{CH_{4}}/N_{CD_{4}}$  can then be expressed as

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$$\frac{{}^{N}CH_{4}}{{}^{N}CD_{4}} = \frac{k_{8}^{H}}{k_{8}^{D}} \left(\frac{\kappa_{3}^{H}}{\kappa_{3}^{D}}\right)^{1/2} \frac{{}^{N}CH_{3}CHO}{{}^{N}CD_{3}CDO}$$
(13)

Substitution of the experimentally determined values for  $N_{CH_4}/N_{CD_4}$  and  $N_{CH_3CHO}/N_{CD_3CDO}$ , and an average value for  $K_3^H/K_3^D$  of 1.43 (2) into eqn. 13, leads to an estimate of  $k_8^H/k_8^D = 1.51$ . The fact that the ratio of  $k_8^H$  to  $k_8^D$  is greater than unity is consistent with the nature of reaction 8, as discussed above. The relationship between  $\theta_{CH_3}$  and  $\theta_{CD_3}$  is obtained very simply. Inspection of eqn. 4 shows that

 $\theta_{CH_3}/\theta_{CD_3} = N_{CH_3CHO}/N_{CD_3CDO}$ , so that  $\theta_{CH_3}/\theta_{CD_3} = 0.5$ . This result is consistent with the projection based on the analysis of eqn. 5 given earlier.

To summarize, the analysis given here indicates that the isotope effects found for acetaldehyde and methane synthesis can be interpreted in terms of a product of equilibrium and kinetic isotope effects. The inverse isotope effect observed for acetaldehyde appears to be due totally to the inverse equilibrium isotope effect associated with the surface coverage by  $CH_3(CD_3)$  groups. In the case of methane, the inverse isotope effect is due to a product of three factors: a normal kinetic isotope effect associated with reaction 8; a normal equilibrium isotope effect associated with the chemisorption of  $H_2(D_2)$ , reaction 3; and the inverse equilibrium isotope effect associated with the surface coverage by  $CH_3(CD_3)$  groups. This last result is consistent with the projection given recently by Wilson (15) and subsequently confirmed by Kellner and Bell (2).

A possible mechanism for the formation of methanol, similar to that recently proposed by Kung (17), is shown in Fig. 6. In this instance it is proposed that CO hydrogenation proceeds without rupture of the C-O bond and that the first stage of this process involves the rearrangement of linearly-adsorbed CO to form a  $\mu$ -bridge adsorbed structure. Species of this type are known to occur in transition metal complexes (18) and can also be formed by interaction of the oxygen of a linearly-bonded CO ligand with a Lewis acid site (19). Furthermore, some evidence for the presence of bridge-adsorbed CO on Ru/Al<sub>2</sub>O<sub>3</sub> has been obtained in recent infrared studies (15). Hydrogenation of the bridge-adsorbed intermediate is postulated to occur initially at the carbon end of the C-O bond. Continuation of this process produces a methoxy species which then undergoes reductive elimination to form methanol.

The results of the present studies of methanol synthesis over  $Ru/Al_2O_3$  do not permit a detailed assessment of the extent to which the mechanism presented in Fig. 6 is correct. Nevertheless, it is significant to point out that the proposed scheme is consistent with two important observations. The first is the occurrence of a substantial increase in the rate of methanol synthesis (see Fig. 4) when  $D_2$ is substituted for  $H_2$  in the synthesis feed. This suggests that one or more of the hydrogenation steps (reactions 4-6 in Fig. 6) is at equilibrium (16). The second observation is that the yield of methanol declines as the flow rate of synthesis gas is reduced (see Fig. 2).

1. 
$$CO + S \neq S - C \equiv O$$
  
2.  $S - C \equiv O + S' \neq S - C \equiv O \cdots S'$   
3.  $H_2 + 2S \neq 2H_s$   
4.  $S - C \equiv O \cdots S' + H_s \neq S - C \equiv O \cdots S'$   
5.  $S - C \equiv O \cdots S' + H_s \neq S - CH_2 - O - S'$   
6.  $S - CH_2 - O - S' + H_s \neq S + CH_3 - O - S'$   
7.  $CH_3 O - S' + H_s \neq CH_3 OH + S' + S$ 

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Fig. 6. Proposed mechanism for the synthesis of methanol.

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As noted earlier, this implies that at lower flow rates the methanol concentration over the catalyst builds up and as a result methanol decomposition enters into competition with the synthesis of this product. Studies by Madix and coworkers have shown that methanol decomposition over Fe, Ni, and Pt (20,21) is initiated by the loss of the hydroxyl hydrogen and the concurrent formation of an adsorbed methoxy structure. Assuming that Ru behaves in a similar fashion to these other group VIII metals and that the concept of microreversability holds, we conclude that the last step in the formation of methanol proceeds as indicated in Fig. 6.

It is not possible at present to explain why acetaldehyde is produced as the primary oxygenated product over the  $Ru/Si0_2$  catalyst while methanol is the primary oxygenated product formed over the  $Ru/Al_20_3$ catalyst. All that one can say is that interactions between the metal and the support alter the catalyst selectivity. Evidence for such effects have also been reported recently by Ichikawa and coworkers (22-25) for Rh, Pd, and Ft catalysts and by Ryndin et al. (26) for Pd catalysts. Unfortunately, the current understanding of the metalsupport interactions is insufficient to warrant speculation concerning the manner in which these interactions affect catalyst activity and selectivity.

#### CONCLUSIONS

The present results demonstrate that under appropriate conditions Ru catalysts exhibits a significant activity for the formation of oxygenated products from CO and  $H_2$ . For  $Ru/SiO_2$  the principal product observed is acetaldehyde. The kinetics of acetaldehyde synthesis and the observation of an inverse  $H_2/D_2$  isotope effect can be explained in terms of a mechanism in which acetaldehyde is formed by insertion of CO across the metal-carbon bond of an adsorbed methyl group followed by reductive elimination of the resulting acetyl group. Comparison of the rate expressions derived for acetaldehyde and methane synthesis, and the  $H_2/D_2$  isotope effects for both products, makes it possible to estimate the individual kinetic and equilibrium isotope effects associated with the synthesis of each product.

When Ru is supported on V-alumina, methanol is produced as the principal oxygenated species. This product readily decomposes back to CO and  $H_2$  and hence the kinetics of methanol formation are sensitive to the methanol concentration in the products. The formation and decomposition of methanol can be explained in terms of a simple mechanism which involves the hydrogenation of  $\mu$ -bridge-adsorbed CO to form a methoxy species. This group then undergoes reductive elimination to form methanol. The observation of an inverse  $H_2/D_2$  isotope effect on the rate of methanol synthesis suggests that one or more of the initial hydrogenation steps is reversible and at equilibrium.

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#### CHAPTER VI

## Effects of Dispersion on the Activity and Selectivity of Alumina-Supported Ruthenium Catalysts for Carbon Monoxide Hydrogenation

#### ABSTRACT

A study was performed to determine the extent to which metal dispersion affects the activity and selectivity of Ru/Al<sub>2</sub>0, catalysts used for CO hydrogenation. For dispersions below 0.7, the specific activity for synthesis of methane and Cor products decreases with increasing dispersion, but neither the probability for chain growth nor the olefin to paraffin ratio is affected. The decrease in activity over this range is ascribed to a decrease in the fraction of sites present on planer surfaces. For dispersions above 0.7, the specific activity for synthesis of all products decreases dramatically, and is accompanied by a slight decrease in the probability of chain growth and a rapid decrease in the olefin to paraffin ratio. These changes are attributed to changes in the electronic properties of the Ru microcrystallites with size and the presence of metal/support interactions. In situ infrared spectra reveal that only those sites that adsorb one linearly bound CO molecule per Ru atom are active for CO hydrogenation. Adsorption of two CO molecules per Ru site is also observed but these sites are catalytically inactive.

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## INTRODUCTION

The influence of dispersion on performance of supported Group VIII metals for the synthesis of hydrocarbons via CO hydrogenation has been studied to only a limited degree. Vannice (1,2) has reported that the specific activity for methanation of Pt and Pd catalysts increases with increasing dispersion; the effect being much more dramatic for Pt than Pd. By contrast, the methanation activity of Ni catalysts was found to decrease with increasing dispersion. Dalla Betta et al. (3) observed a similar trend for  $\operatorname{Ru}/\operatorname{Al}_2O_3$  catalysts. In a more detailed study, King (4) reported that the specific activities of supported Ru catalysts for methanation and CO consumption decreased monitonically with increasing Ru dispersion. No correlation was noted, though, between the distribution of hydrocarbon products and dispersion.

In the present study, an investigation of the effects of dispersion on the characteristics of  $Ru/Al_2O_3$  catalysts for hydrocarbon synthesis was undertaken. Emphasis was placed on defining the effects of Ru dispersion on specific activity, product distribution, and olefin to paraffin ratio of the products. In addition to analysis of reaction products, <u>in situ</u> infrared spectroscopy was used to characterize the structure of chemisorbed CO as a function of catalyst dispersion.

#### **EXPERIMENTAL**

Three v-alumina-supported catalysts were used in this investigation. A  $1.3\% \text{ Ru/Al}_2O_3$  catalyst was prepared by adsorption of  $\text{Ru}_3(\text{CO})_{12}$  from pentane solution (5). The dried catalyst was reduced in flowing H<sub>2</sub> at 1 atm. Reduction was begun by raising the temperature from 298 to 673K after which the temperature was maintained at 673K for 8 hr. The dispersion of the reduced catalyst was measured by H<sub>2</sub> chemisorption and determined to be 0.9. Two catalysts, a 3.0%  $\text{Ru/Al}_2O_3$  and an 11%  $\text{Ru/Al}_2O_3$  catalyst were prepared by incipient wetness impregnation of the support with an aqueous solution of  $\text{RuCl}_3$ , acidified to pH = 2 to suppress hydrolisis. The resulting slurry was air dried and then heated slowly in vacuum from 298 to 423K. Reduction of these catalysts was carried out using the procedure described for the 1.3%  $\text{Ru/Al}_2O_3$  catalyst. The dispersion of the 3.0%  $\text{Ru/Al}_2O_3$  catalyst, was 0.3.

Investigations of catalyst activity were conducted at 1 and 10 atm. The lcw pressure studies were carried out in a glass microreactor connected to a glass vacuum and gas handling system. The design of this apparatus allowed measurements of synthesis activity and  $H_2$  isotherms to be performed in the same cell. The flow of synthesis gas a preblended  $H_2/CO$  mixture  $(H_2/CO = 2)$  - to the reactor was controlled by a needle value and measured using a bubble flow meter. Analysis of the reaction products was carried out by gas chromatography using flame ionization detection of the eluted components. Products in the  $C_1$  through  $C_5$  range were separated using a 1 m x 2.4 mm stainless steel

column packed with Chromosorb 106. A 2.5 cm<sup>3</sup> sample was injected into the column maintained at 318K. The column temperature was then programmed to 478K at 10K/min. Separation of C<sub>4</sub> through C<sub>14</sub> products was carried out using a 50 m x 0.25 mm fused silica, WCOT, column with SZ-54 liquid phase. A modified Grob injection (6) was used to introduce the sample. With the column at 193K, a 10 cm<sup>3</sup> gas sample was injected at a split ratio of 20:1. The column was held at 193K for 5 min and then programmed at 5K/min to 478K.

High pressure studies were conducted in a stainless steel microreactor which also served as an infrared cell. The design of this cell is similar to that recently described by Hicks et al. (7). Synthesis gas was supplied to this reactor from a high pressure manifold and products were analysed by gas chromatography. These portions of the apparatus have been described previously (8,9).

Infrared spectra were taken with a Jigilab FTS-10M Fourier Transform infrared spectrometer at a resolution of 4 cm<sup>-1</sup>. Typically, 100 interfereograms, each acquired in 1.25 s, were co-added to improve the signal to noise racio. In addition to recording spectra of the catalyst under reaction conditions, spectra were also recorded of the catalyst following reduction in  $H_2$  and of a support disc, placed downstream of the catalyst disc, during reaction. The latter two spectra were used to subtract out infrared absorptions due to the support and the gas phase.

#### RESULTS

## Catalyst Activity and Selectivity

Experiments conducted with the 1.3% Ru/Al<sub>2</sub>O<sub>3</sub> catalyst revealed that the dispersion of this catalyst decreased under reaction conditions from its initial value of 0.9. To determine how the progressive change in metal dispersion affected the activity and selectivity of the catalyst, a series of short duration runs were performed at 1 atm in the cell used to obtain H, isotherms. Approximately 800 mg of the catalyst was heated to 623K at 1K/min and then maintained at 623K for 2 br. Following reduction, the cell was again evacuated and the temperature was reduced to 373K. An H, isotherm was then determined at 373K. Next, the cell was once more evacuated and, after reducing the temperature to 297K, a preblended  $H_0/CO$  mixture ( $H_0/CO = 2$ ) was passed over the catalyst at 1 atm and 100 cm<sup>3</sup>/min (NTP) for 10 min. At the end of this time, the coll temperature was increased to 477K over a 5 min interval. After 20 min at temperature, gas samples were taken for analysis. The reaction was then terminated and the cell evacuated. The catalyst was then reduced, following the procedure described earlier, and a new H, isotherm was determined in preparation for a subsequent reaction run. The complete procedure was repeated six times, at the end of which it was observed that the catalyst had attained a relatively stable dispersion of 0.6. Similar reaction andreduction cycles were also carried out with a 50 mg sample of the 11% Ru/Al203 catalyst. The activity of this catalyst was stable and, therefore, it was assumed that the catalyst dispersion did not decrease with use. It should be noted that in all instances the conversion of CO never exceeded 2% with either catalyst.

The effect of dispersion on the turnover number for methane synthesis,  $N_{C_1}$ , is shown in Fig. 1. With the exception of the point for  $D_{Ru} = 0.3$ , which was obtained using the 11%  $Ru/Al_2O_3$  catalyst, all of the data were collected using the 1.3%  $Ru/Al_2O_3$  catalyst. The points plotted in Fig. 1 are based on the average dispersion pertaining to a 20 min period of reaction. In those cases where a change in dispersion occurred during a reaction cycle, the initial and final dispersions are indicated by error bars. The results presented in Fig. 1 clearly show that as dispersion increases, the turnover number for methane synthesis rapidly declines. It is also apparent that the data lie along two line segments that meet near  $D_{Ru} = 0.75$  and that the absolute magnitude of the slope of the segment for  $D_{Ru}^{>0.75}$ .

For the sake of comparison with the present results, King's data (4) for unsupported Ru and for alumina-supported Ru have also been shown in Fig. 1. It is evident that the data for both the supported and unsupported metal lie along a common line and that the slope of that line is nearly identical to that obtained in the present study for catalysts with Ru dispersions below 0.75. The vertical displacement of King's data is due to the higher pressure and temperature used in his study.

Figure 2 shows that, with decreasing dispersion, the specific activity for the synthesis of  $C_2$  through  $C_{14}$  hydrocarbons increases in a manner similar to that observed for methane. In this figure, the



Fig. 1. Effect of dispersion of alumina-supported Ru on the specific activity for methane formation.



Fig. 2. Effect of dispersion on the rates of formation of hydrocarbon products over alumina-supported Ru.

turnover number,  $N_{C_n}$ , for producing a product containing n carbon atoms, is based on the dispersion determined at the end of a 20 min period of reaction. Note that for each dispersion the majority of the points lie along a straight line on the coordinates of  $ln(N_{C_n})$  versus (n-1), as would be expected if chain growth occurs via a step-wise polymerization type mechanism (9,10). The only points that fail to lie along the straight lines are those for n = 2 and for n > 13.

Figure 3 shows that the extent of deviation of the points for n > 13, from a log-normal product distribution, strongly depends on the reactant flow rate and the time at which a product sample is taken for analysis. As either the flow rate or the time of reaction is increased, the extent of deviation decreases significantly. Similar observations were also made for runs conducted at 10 atm, in which case deviations from a log-normal product distribution were seen for n > 5.

The slope of the straight lines shown in Fig. 2 is equal to  $\log \alpha$ , where  $\alpha$  is the probability of hydrocarbon chain growth (9,10). Table I shows that the magnitude of  $\alpha$  increases slightly from 0.63 to 0.7 as the dispersion, measured after reaction, decreases from 0.82 to 0.67. Thereafter,  $\alpha$  remains constant at a value of about 0.7.

Figure 4 illustrates the effect of dispersion on olefin to paraffin ratio of products containing 2, 4, 6, 8, and 10 carbon atoms. In each case the ratio,  $N_{C_n} / N_{C_n}$ , is found to be weakly dependent on dispersion for dispersions below about 0.6 to 0.7. For higher dispersions, the ratio drops precipitiously, indicating the formation of a very paraffinic product. While not shown, similar results were obtained for products containing 3, 5, 7, 9, 11, 12, 13, and 14 carbon atoms.



Fig. 3. Effects of flow rate and time of reaction on the rates of formation of hydrocarbon products over alumina-supported Ru.

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i	D <sub>Ru</sub> <sup>(i-1)<sup>b</sup></sup>	(i) <sup>c</sup> D <sub>Ru</sub>	. a '
1	0.90	0.82	0.63
2	0.82	0.80	0.66
3	0.80	0.73	0.69
4	0.73	0.67	0.70
5	0.67	0.64	0.71
6	0.64	0.60	0.70
7 <sup>d</sup>	0.3 .	- · ·	0.69

Table I. Effects of Dispersion on the Probability of Chain Growth<sup>a</sup>

<sup>a</sup>Reaction Conditions: T = 479K; P = 1 atm; H<sub>2</sub>/CO = 2 Catalyst: 1.3% Ru/Al<sub>2</sub>O<sub>3</sub>. <sup>b</sup>Measured before reaction cycle i

c<sub>Measured</sub> after reaction cycle i

<sup>d</sup>Catalyst: 11% Ru/Al<sub>2</sub>0<sub>3</sub>



Fig. 4. Effect of dispersion on the olefin to paraffin ratio of hydrocarbon products for n = 2, 4, 6, 8, 10 over alumina-supported Ru.

#### Infrared Spectroscopy

Figure 5a shows a series of spectra taken under reaction conditions, using the 1.3% Ru/Al<sub>2</sub>03 catalyst. The procedure used to obtain these spectra was as follows: A freshly prepared catalyst disc was reduced in situ in flowing  $H_2$  at 573K and 10 atm for approximately 16 hr. The temperature was then reduced to 498K and a 3/1 H $_2/CO$  mixture was fed to the reactor. Reaction was allowed to proceed for 10 min. During the last 2 min of this period 100 interfereograms were taken of the catalyst and co-added. At the end of the reaction period, a gas sample was taken for analysis and the flow of synthesis gas was replaced by a flow of H,. After 10 min of reduction a second series of interferograms were taken. Reduction was then continued for an additional 40 min at which time the flow of synthesis gas was restored. The spectra of the catalyst taken after 10 min of reduction are shown in Fig. 5b. The reaction and reduction cycle was repeated a total of seven times. Spectra for six of these cycles are shown in Fig. 5 experimental difficulties precluded obtaining spectra for the fourth cycle. At the end of the seventh cycle, the catalyst was exposed to a flow of CO at 2.5 atm and 473K for 8 hr and then reduced in flowing H, at 10 atm and 573K for 12 hr. Following this procedure, a regular reaction/reduction cycle was carried out. Spectra 7a and 7b characterize the catalyst for this case.

The spectra taken under reaction conditions, illustrated in Fig. 5a, exhibit a broad band centered near 2000 cm<sup>-1</sup> and two sharper bands located at 2040 and 1960 cm<sup>-1</sup>. On the basis of previous studies (11 - 13), these bands can be assigned to linearly adsorbed CO; the

Fig. 5 Infrared spectra obtained during successive reaction - reduction cycles using the 1.3% Ru/Al<sub>2</sub>0<sub>3</sub> catalyst: a) during reaction at 498K, 10 atm, H<sub>2</sub>/CO = 3; b) following reduction in H<sub>2</sub> at 10 atm and 498K for 10 min; c) difference between the spectra taken under the conditions given in a) and b); Spectra 1-3 correspond to cycles 1-3; spectra 4-7 correspond to cycles 5-8; Between cycles 7 and 8 the catalyst was exposed to 2.5 atm of CO at 473K and then reduced in 10 atm of H<sub>2</sub> at 573K for 12 hr.



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Fig. 5.

broad central band to mono-adsorbed CO (Ru-CO) and the bands at 2040 and 1960 cm<sup>-1</sup> to a di-adsorbed species (OC-Ru-CO) associated with either isolated Ru atoms or small Ru clusters that interact strongly with oxygen atoms in the support (5,13). A complementary study (13) revealed that the di-adsorbed form of CO is quite stable to  $\Pi_2$  reduction at temperatures below 548K. As a consequence, it is possible to subtract the spectra appearing in Fig. 5b from those presented in Fig. 5a. The resulting spectra, shown in Fig. 5c, provide a clearer view of the spectrum of mono-adsorbed CO. The position of the band maximum can now be established as approximately 2010 cm<sup>-1</sup>.

As the catalyst is cycled between reaction and reduction conditions, the intensities of the bands shown in Fig. 5 decline. This trend is also seen in Table II which lists the integrated band intensities observed during each cycle. The rate of methane formation ratioed with respect to the total number of Ru atoms present in the catalyst is also given in Table II. This figure is seen to increase by nearly 3.5 as the catalyst is cycled. Taken together with the infrared observations, these data indicate that the specific activity of the catalyst increases as the Ru dispersion decreases, in a manner similar to that shown in Fig. 1.

Infrared spectra were also obtained using the  $3.0\% \text{ Ru/Al}_2^{0}_3$  catalyst. Figure 6a illustrates the spectra obtained both under reaction conditions and following H<sub>2</sub> reduction. For the sake of comparison, spectra taken with the  $1.3\% \text{ Ru/Al}_2^{0}_3$  catalyst, following attainment of a stable catalytic activity, are shown in Fig. 6b. Under reaction conditions, the band for mono-adsorbed CO at 2010 cm<sup>-1</sup> is



Fig. 6. Infrared spectra obtained under reaction conditions and following reduction: a) 3.0% Ru/Al<sub>2</sub>O<sub>3</sub>; b) 1.3% Ru/Al<sub>2</sub>O<sub>3</sub>; Spectrum 1 is taken during reaction at 473K, 10 atm, H<sub>2</sub>/CO = 3; Spectrum 2 is taken following reduction in H<sub>2</sub> at 10 atm and 473K; Spectrum 3 is the difference between spectra 1 and 2.

nearly identical for both catalysts. The bands at 2040 and 1960 cm<sup>-1</sup> associated with di-adsorbed CO, are much less intense, though, for the  $3.0\% \text{ Ru/Al}_{2}0_3$  catalyst. These results, as well as those presented in Fig. 5, strongly suggest that it is only the mono-adsorbed form of CO that participates in the hydrogenation of CO to form hydrocarbons.

The rate jata taken in conjunction with the infrared spectra presented in Fig. 5 can also be used to illustrate the correlation between the specific activity of Ru for methane synthesis and the metal dispersion. To do so, it is first assumed that the integrated absorbances of the bands presented in Figs. 5b and 5c are proportional to the surface coverages by mono- and di-adsorbed CO, respectively. This assumption has recently been verified for mono-adsorbed CO by Winslow et al. (14) using a silica-supported Ru catalyst. For the di-adsorbed form, this assumption can be inferred from the results presented by Yates et al. (15) for alumina-supported Rh. Next, it is assumed that the proportionality factors, per CO moiety, between integrated absorbance and surface concentration are the same for both forms of adsorbed CO. While this assumption has not been substantiated for Ru, it does appear to be valid for Rh (15). The catalyst dispersion at the end of each reaction cycle can now be determined by

$$D_{Ru}^{(i)} = D_{Ru}^{(1)} \qquad \frac{A_{M}^{(i)} + 0.5 A_{D}^{(i)}}{A_{M}^{(1)} + 0.5 A_{D}^{(1)}} \qquad (1)$$

where  $D_{Ru}^{(i)}$  is the Ru dispersion and  $A_M^{(i)}$  and  $A_D^{(i)}$  are the integrated absorbances for the mono- and di-adsorbed forms of CO, respectively. The superscript i represents the cycle number.

The specific activity at the end of each cycle can be determined from the rates given in Table II and the values of  $D_{Ru}^{(i)}$  given by eqn. 1. The value of  $D_{Ru}^{(1)}$  has been assumed to be equal to 0.8. The values of N<sub>C1</sub> obtained in this manner are presented in Table II and illustrated by the square symbols plotted in Fig. 1. Inspection shows that, here too, the point lie along a straight line, the slope of which is nearly the same as those determined for the other two data sets.

# DISCUSSION

The data presented in Figs. 1 and 2 clearly demonstrate that the specific activity of Ru for hydrocarbon synthesis declines with increasing dispersion of the metal. A modest decrease in specific activity is observed for dispersions of less than about 0.75 and a much more rapid decrease is found for higher dispersions. Figure 1 also shows that over the lower dispersion range, the slope of the decrease in specific activity with dispersion found in the present studies, is in excellent agreement with that observed by King (4). Moreover, it appears that, over the range of temperatures and reactant partial pressures examined, the slope is nearly independent of reaction conditions.

A plausible explanation for the decrease in specific activity with increasing dispersion, observed for  $0.3 > D_{Ru} > 0.75$ , is that the fraction of the surface sites suitable for carrying out the hydrogenation of CO, decreases with the dispersion. Such a trend would be observed if the reaction requires sites present on the planer surfaces of Ru crystallites (16-19). Calculations by Van Hardeveld and Hartog (17,18) indicate that, for particles between 37 and 12 Å in average size corEffects of Dispersion on the Integrated Band Intensities for Adsorbed CO and the Activity for Methane Synthesis<sup>a</sup> Table II.

	-4	4-	4-		4	-4	4	
(i NC <sub>1</sub> (s <sup>-1</sup> )	2.81 x 10	6.67 x 10	9.62 × 10	1	15.1 x 10	15.8 x 10	16.7 × 10 <sup>-</sup>	22.8 × 10
D <sub>Ru</sub> (i)d	0.80 <sup>e</sup>	0.60	0.55	۱.	0,46	0.44	0.43	0.34
r <sub>61</sub> (s <sup>-1</sup> ) <sup>c</sup>	2.25 x 10 <sup>-4</sup>	4.00 × 10 <sup>-4</sup>	5.29 × $10^{-4}$	6.14 x 10 <sup>-4</sup>	6,9 x 10 <sup>-4</sup>	6.96 × 10 <sup>-4</sup>	7.19 x 10 <sup>-4</sup>	$7.75 \times 10^{-4}$
$A_{M}^{(i)}/(A_{M}^{(i)} + 0.5A_{D}^{(i)}$	0.79	0.75	0.78		0.76	0.75	0.77	0.84
(i)b A <sub>D</sub>	2.25	2.00	1.60	п.а.	1.45	].47	1.37	0.70
(i)b A <sub>M</sub>	4.20	3.00	2.85	n.a.	2.35	2.18	2.18	1.88
1		7	e	4	2	9	7	8

<sup>a</sup>Catalyst - 1.3% Ru/Al $_{2}$ O<sub>3</sub>; T = 498K; P = 10 atm;  $N_{2}$ /CO = 3

<sup>b</sup>Arbitrary units

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CBased on total number of Ru atoms

dFrom eqn. l

eAssumed

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 $f_{N_{C_1}} = r_{C_1} / D_{R_u}^{(i)}$ 

Brollowing exposure to 2.5 atm CO at 473K for 8 hr and subsequent reduction in N2 at 10 atm and 573K for 12 hr

responding to  $0.3 > D_{Ru} > 0.75$ , the fraction of sites associated with planer surfaces deckeases by a factor of about 3 to 4. This decrease is smaller than the observed decrease in specific activity - a factor of 7.5 - but, nevertheless, is of the same order of magnitude. A further test of the proposed interpretation can be made by comparing the ratio of specific activities and the fraction of planer sites for  $D_{Ru} = 0$  and  $D_{Ru} = 0.75$ . The data presented in Fig. 1 indicate that the activity ratio is about 25. On the other hand, the ratio of the fractions of planer sites, determined for h.c.p. truncated bipyrimids (17), is 20. Thus, here too there is a reasonable level of consistancy.

An alternative interpretation, and the one originally proposed by King (4), is that the decrease in specific activity with increasing dispersion may be due to changes in the electronic properties of the particles. Several reasons can be identified for ruling out this explanation. To begin with, theoretical studies (19-23) of the electronic properties of small metal particles show that deviations from the properties of bulk metal occur, primarily, for crystallites smaller than about 20 Å. This critical size corresponds to a dispersion of about 0.5. If electronic effects are assumed to be central to the change in the specific activity of the catalyst, then it would be expected that these effects would be evidenced primarily for  $D_{Ru}^{}$  < 0.5. Figure 1 shows this not to be the case and, in fact, the specific activity continues to rise smoothly as  $D_{Ru}$  decreases to zero. A second argument for excluding an interpretation based on electronic effects can be made on the basis of the infrared studies presented here. The spectra in Fig. 5 show that the vibrational frequency of mono-adsorbed

CO (see Fig. 5) is independent of dispersion; contrary to what would be anticipated if the electronic properties of the particles change to a significant degree with particle size (19).

For dispersions greater than about 0.7, the specific activity and olefin to paraffin ratio of the products undergo a very rapid decrease with increasing dispersion and the probability of chain growth,  $\alpha$ , decreases slightly. At such high dispersions, the average Ru particle size is less than 12 Å, and, as a result, a substantial fraction of the particles fall within a size range where particle size and metalsupport interactions can influence the electronic properties of the particles (19-23). One of the effects that might be expected to occur is a reduction in the density of electronic charge in the d-orbitals protruding from the metal surface. This could lead to a reduction in the degree of back-donation of charge from these orbitals to the  $\pi^{-}$ antibonding orbitals of chemisorbed CO and, in turn, reduce the degree to which the C-O bond is weakened (10,24). Since the dissociation of molecularly adsorbed CO is considered to be a critical step in the mechanism of hydrocarbon synthesis over Ru (10,25), and since dissociative chemisorption of CO is facilitated by charge transfer to the  $\pi^{\star}$  orbital of adsorbed CO, a reduction in the back donation of d-electrons could be regarded as cause for reducing catalyst activity. The decreases in  $\alpha$  and olefin to paraffin ratio are probably due to other electronic effects, as yet not clearly defined.

It is clear from Fig. 2 that over the range of dispersions considered in this investigation, the majority of the products distribute along straight lines on plots of  $\ln (N_{C_n})$  versus (n-1). As discussed
by a number of authors (9,10,25-28), such plots suggest that the growth of hydrocarbon chains occurs via the stepwise addition of C, units. Deviation of the point for C, hydrocarbons from the linear distribution. can be ascribed to a partial hydrogenolysis of these products to methane (9). The data presented in Fig. 3 show that the deviation for the C121 products is sensitive to the flow rate of synthesis gas and to the duration between the initiation of reaction and product analysis. The decrease in the deviation as either the flow rate or the time of reaction is increased suggests that the deviation is caused by a partial adsorption of C12+ hydrocarbons on the support. This interpretation is supported by infrared observations (11,13) that show a progressive accumulation of hydrocarbons on the support during reaction. By increasing the flow rate of the feed gas, the concentration of hydrocarbons in the gas phase over the catalyst is reduced, and with it, the equilibrium loading of the support. As a consequence, the time required to achieve the equilibrium loading is reduced.

The results presented in Fig. 3, together with the discussion given above, indicate that over the range of dispersions studied here, there is no indication of a cutoff in chain growth associated with particle size, as has recently been suggested by Nijs and Jacobs (29,30). While it is possible that such a cutoff could exist for particles so small that the normal kinetics of chain growth are distorted by the limited availability of  $C_1$  monomer units, clear evidence for such an effect is not yet available. Moreover, the results of this investigation suggest that very high dispersion catalysts would exhibit extremely low specific activities.

In the present studies the number of surface Ru sites has been determined by  $H_2$  chemisorption assuming a stoichiometry of one H-atom per surface Ru atom. The infrared results presented in Figs. 5 and 6 suggest, though, that only those sites that adsorb a single CO molecule per site are active in hydrocarbon synthesis. The sites that adsorb two CO molecules per site appear to be catalytically inactive over the temperature range investigated here; conclusions identical to those presented previously (13), based on a detailed infrared study of CO chemisorption on Ru/Al<sub>2</sub>O<sub>3</sub> catalysts. Based on the assumption that the extinction coefficients for mono-adsorbed and di-adsorbed CO are equal, the data presented in Table II suggest that roughly 80% of the surface sites are active and, hence, that the specific activities presented in Figs. 1 and 2 are a factor of 1.25 too low.

The data in Fig. 2 indicate further that as the 1.3% Ru/Al<sub>2</sub>O<sub>3</sub> catalyst sinters under reaction conditions, the fraction of monoadsorbed CO remains nearly constant. However, extended exposure of the catalyst to CO at elevated temperatures reduces this fraction significantly. The mechanism of Ru sintering is not revealed by these observations, but the trends in band intensities reported in Table II suggest that under reaction conditions the metallic particles grow by the agglomeration of both small clusters and metal crystallites. Both processes must be operative if one is to explain the simultaneous attenuation of the integrated absorbances for mono-adsorbed and diadsorbed CO, while maintaining a nearly constant ratio of the two adsorbate forms. It is concievable that the very rapid growth in average particle size observed during CO hydrogenation is facilitated by the

exothermicity of the reaction. The release of heat on a particle surface may give rise to an elevation of the particle temperature well above the average reaction temperature. If this occurs, the particle could migrate more readily across the support surface than if the particle temperature remained at the average catalyst temperature. At the same time, one might envision the release of individual Ru atoms from small Ru clusters and migration of these atoms to a growing microcrystallite. Small clusters would contribute to such a process more readily than larger crystallites since the metal-metal bond energy decreases significantly with decreasing particle size (20). These proposed mechanisms of sintering are admittedly speculative and are not supported by independent evidence. It is anticipated, though, that a better interpretation will be possible following further study of this problem.

### CONCLUSIONS

The dispersion of Ru on an alumina support has a pronounced effect on the activity of Ru for CO hydrogenation. For dispersions below about 0.7, there is a moderate decrease in the specific activity for synthesis of methane and  $C_{2+}$  hydrocarbons with increasing dispersion, but neither the probability of chain growth not the olefin to paraffin ratio of the products is greatly affected. Dispersions above 0.7 exhibit a very rapid decline in the turnover frequencies for the synthesis of all products. This is accompanied by a slight decrease in the chain growth probability and a very dramatic decrease in the olefin to paraffin ratio. At all dispersion levels, the distribution of hydrocarbon products with number of carbon atoms is of a log - normal

type. The decrease in specific activity with increasing dispersion, for dispersions below 0.7, is attributed to a decrease in the fraction of sites present on the planer surfaces of the Ru microcrystallites; while the much faster decrease in specific activity, observed for dispersions greater than 0.7, is believed to be due to changes in the electronic properties of the small crystallites with size or resulting from interactions of the crystallites with the support. <u>In situ</u> infrared spectra suggest that only those Ru sites that adsorb one linearly-bound CO molecule per site are active for CO hydrogenation, whereas those adsorbing two CO molecules per site are not active under the conditions used in this study.

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### CHAPTER VII

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### APPENDIX I

### Experimental Methods - Apparatus and Procedures

The experimental apparatus consists of a flow system, a microreactor, an infrared reactor, and gas chromatagraphs for product analysis. Each of these components and special procedures associated with its use are described below.

### Flow System

A schematic of the flow system is presented in Fig. 1. This system is designed for operation at pressures between 1 and 30 atm. The flow rate of each gas is controlled by micro-metering values and is measured by monitoring the pressure drop produced across a fixed capillary tube. Provisions are also available for injecting 1 cm<sup>3</sup> aliquots of a particular component into a steady flow going to the reactor.

The gases used for the majority of the reaction studies are  $H_2$ (LBL, > 99.999%), He(LBL, > 99.995%), and CO(Matheson UHP, > 99.8%). Preblended  $H_2$ /CO mixtures prepared and analysed in the laboratory are also used. Ethylene (Matheson CP, > 99.5%) and  $D_2$  (LBL, > 97.5%) have also been used on occasion as components of the synthesis gas feed. Helium and  $H_2$ /CO mixtures are purified by passage through molecular sieve traps maintained at 195K to remove water and metal carbonyl contaminants. Prior to passage through the molecular sieve trap, the  $H_2$ is passed through a Natheson Deoxo unit to remove oxygen.

The use of preblended  $H_2/CO$  mixtures insures that gas compositions are accurate and consistant for all runs. Mixtures are prepared by



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Fig. 1. Schematic of the high pressure flow system.

requential addition of each pure component into an evacuated cylinder to the desired partial pressure. The base of the cylinder is then heated with a heating tape to provide convective mixing of all components present in the cylinder. The composition of the mixture is analysed by gas chromatography. The concentrations of CO and any hydrocarbons that have been added are determined by comparison of the measured peak areas with those obtained with known standards. The H<sub>2</sub> concentration is determined by difference. If the mixture does not meet the desired composition, more of the deficient components are added and the mixing and analysis procedures are repeated. Mixture compositions accurate to  $\pm 0.5\%$  of the desired value are obtained in this manner.

### Microreactor

A microreactor, 4.9 mm in diameter by 50 mm in length, constructed of stainless steel tubing and Swageloc fittings is utilized in all runs in which accurate kinetic data, are desired. In order to provide adequate heat transfer to and from the catalyst, the reactor is submerged in a heated and fluidized sand bath, as shown in Fig. 1. The catalyst is contained by plugs of quartz wool and its temperature is measured with a stainless steel sheathed thermocouple placed in the catalyst bed. The small fluidized sand bath in which the reactor is placed, is heated by means of cartridge heaters present in the lower third of the bath, and maintained at reaction temperature with a time proportioning temperature controller. The temperature difference between the catalyst bed and the sand bath is normally less than IK.

### Infrared Reactor

A schematic of the cell utilized for <u>in situ</u> infrared studies of the catalyst during reaction is presented in Fig. 2. The infrared reactor consists of two such cells connected in series. A catalyst wafer is placed in the first cell and a wafer of the support material alone is placed in the second cell. By ratioing the spectra obtained with these two cells, peaks due to absorbances in the gas phase can be minimized, thus allowing spectra of species adsorbed on the catalyst surface to be observed. By minimizing the gas path through which the IR beam must pass, reasonable spectra could be obtained at high pressures.

The reactor is heated by means of etched-foil heating elements (Thermal Circuits Inc.) placed on the faces of each cell. Sheathed thermocouples placed near the catalyst and reference discs are used to monitor the temperature of each cell and a time proportioning temperature controller is used to control the reactor temperature. The reactor temperature can be maintained to within  $\pm$  IK of the desired value; however due to the possibility of infrared and radient heat transfer to or from the catalyst, the temperature of the catalyst *is* known with less accuracy.

There are two areas where sealing techniques are of significant importance in this reactor design: i) the main seal between the two cell flanges and ii) the critical seal between the IR transparent windows and the cell body. The main seal between the two flanges of each cell is accomplished by means of knife edges that bite into a copper gasket. The IR transparent windows are sealed into each flange with



Fig. 2. Schematic of the high pressure infrared reactor.

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Vac Seal (Space Environmental Laboratories). The material of the IR transparent windows and technique used to provide a seal between the window and cell body determine the severity of conditions at which the reactor can be operated. This reactor utilizes polycrystalline CaF<sub>2</sub> windows (Harshaw Chemical), 7 mm thick by 25 mm in diameter, with an unsupported diameter of 16 mm. The windows limit the reactor pressure to approximately 100 atm while the use of Vac Seal limits the operating temperature to below 575 to 625K.

The seal between the cell body and CaF<sub>2</sub> windows is achieved by applying a layer of Vac Seal to each flange where they come into contact with the window face; bringing the window and cell body into intimate contact and allowing the bond to cure for a minimum of 176 hr at 298 K and an additional 48 hr at 373K. Because Vac Seal remains pliable at high temperature, a slight positive pressure should be maintained within the reactor to help insure that an adequate seal is maintained between the windows and cell body. It has been found, though, that the reactor can be operated at 1 atm for short periods of time with no apparent adverse effects.

For <u>in situ</u> infrared studies, the catalyst and support material are ground into very fine powders, in order that light scattering is minimized, and pressed into self-supporting wafers. Wafers are formed by placing 60 to 100 mg of the finely divided powder in a dual piston type die with a split retaining sleeve; rotating the upper portion of the die to evenly distribute the powder; and applying  $5 \times 10^7$  to  $5 \times 10^8$  Pa to the die. The split retaining ring is then removed from the die and the pressure released. The pressure used in this procedure

is the minimum that results in a wafer of adequate mechanical strength. If, on examining the wafer, any cracks are observed, it should be discarded. Gracks will transmit a much higher fraction of the incident radiation than the rest of the wafer resulting in poor quality spectra. Typically, less than 5% of the incident radiation is transmitted by these wafers.

### Product Analysis

A Varian 3700 series gas chromatagraph equipped with a gas sampling valve, dual 1 m x 2.4 mm Chromosorb 106 columns, and flame ionization detectors, is used to analyse the reactor effluent for  $C_1$  through  $C_5$  paraffins and olefins, methanol, and acetaldehyde. Sampling to this chromatagraph is through a gas sampling valve connected in the effluent line from the reactor. A 1 ml gas sample is injected into the column while its temperature is held at 318K. The column oven is then temperature programmed at 10K/min to 498K. The absolute concentration of each hydrocarbon component is calculated by comparing its peak area, determined by disc integration, to the area obtained with a calibration gas of known composition. Because an accurate calibration mixture with methanol and acetaldehyde is not available in this laboratory, concentrations of these products are determined from their peak areas and their response factors relative to that for the combined  $C_3$  components present in the calibration mixture.

Analysis of  $C_4$  through  $C_{14}$  hydrocarbons is performed by capillary gas chromatography using either a Varian 3700 or Perkin-Elmer Sigma 3b gas chromatagraph. The first of these instruments contains a glass 35 m x 0.25 mm, OV-101 WCOT column and the second a fused silica,

50 m x 0.25 mm, SE-54 WCOT column. Both instruments can be temperature programmed from 183K and have flame ionization detectors. Sample introduction is by a modified Grob injection technique, although, because of hardware differences, the technique is slightly different with each chromatagraph. While maintaining the column oven at 193K, a 10 ml gas sample is injected into the capillary splitter, by means of a gas tight syringe, over a 15 sec time interval. With the Varian instrument, the splitter is kept closed during this procedure and during a subsequent period of 45 sec, while with the Perkin-Elmer instrument, a split ratio of 20:1 is maintained at all times. The column oven is maintained at 193K for 5 min and then programmed at 5K/min to 473K. A representative chromatogram obtained with the Perkip-Elmer instrument is presented in Fig. 3. Relative product concentrations obtained from electronic integration of peak areas are independent of which chromatograph is used. Peak identifications are made by gas chromatography/ mass spectrometry analysis employing columns and temperature programs similar to those used in the laboratory. Normal paraffins and a-olefins are easily identified but peaks due to isomers of these products are not easily assigned to specific structures. For this reason, isomeric products are identified by their molecular weight and carbon to hydrogen ratio only. Identifications within each carbon number group are similar to those shown for  $C_{g}$  components in Fig. 3.

Complete hydrocarbon product distributions are determined by normalizing the  $C_4$  or  $C_5$  peak areas obtained in the two analysis, assuming that the FID response factors are independent of structure for products observed using the capillary analysis.





Sample: modified Grob injection, 10 ml gastight syringe Temperature Program: initial temp: 193K

Detector: FID

time: 5 min

Instrument: Perkin-Elmer Sigma 3b Column: fused silica SE-54 WCOT capillary Carrier Gas: He; P = 270 kPa; split ratio = 20:1

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### APPENDIX II

### Chemisorption-Apparatus and Procedures

### ApparaLus

The volumetric apparatus utilized in determining  $H_2$  and CO adsorption isotherms, described in Fig. 1, is constructed mainly of pyrex with a combination of non-greased teflon valves and greased, evacuable, glass stopcocks. It is equipped with two pumping systems: i) a mechanical pump for roughing and, ii) an oil diffusion pump equipped with a separate mechanical pump, for final evacuation of the catalyst prior to obtaining an isotherm. All pumps are isolated by liquid N<sub>2</sub> cooled traps., The residual gas pressure obtained with the oil diffusion pump is measured with a Bayard-Alpert type ionization gage while pressures obtained during adsorption measurements are monitored with a Baracel capacitance type pressure transducer accurate to 1 pa. The pyrex adsorption cell, that can also be utilized as a differential flow reactor, is heated in an electronically controlled furnace and is attached to the system with Cajon ultratorr fittings.

### Gases

Hydrogen (Matheson UHP, > 99.999%), utilized for catalyst reduction and adsorption measurements, is purified by passage through a Deoxo unit to remove  $0_2$  and through a molecular sieve trap cooled to 78K for removal of  $H_20$ . Carbon monoxide (Matheson UHP, > 99.8%) and helium (LBL, > 99.998%) are purified by passage through molecular sieve traps maintained at 195 and 78K respectively.



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Fig. 1. Schematic of volumetric adsorption apparatus.

### Procedure

A catalyst charge of approximately one gram is placed in the adsorption cell, evacuated, and heated to 425K to remove absorbed  $H_2^{0}$ . After cooling the catalyst to 298K, a flow of  $H_2$  is passed over the catalyst and the temperature increased at 1K/min to the desired maximum reduction temperature (623 or 673K). This temperature is then maintained for a minimum of 4 h. Next, the catalyst is evacuated to a pressure of less than 2 x 10<sup>-3</sup> pa. Subsequently, the catalyst temperature is reduced to 373 or 298K depending on whether a  $H_2$  or CO isotherm is to be determined.

An isotherm is obtained, following procedures similar to those described by others (1,2), by sequentially admitting small aliquots of gas to the adsorption cell from the dosing volume. This volume consists of the calibrated volume plus a secondarily calibrated volume consisting of the section of the manifold where the pressure transducer is located. The temperature and pressure of the dosing volume and the adsorption cell are recorded before and after each dose. The process is repeated until a residual pressure of approximately  $5 \times 10^4$  pa is obtained. After the adsorption data have been obtained, the catalyst is evacuated and an aliquot of He is admitted to the cell in order that the effective volume of the adsorption cell can be estimated at the temperature of the adsorption measurements.

An adsorption isotherm is obtained by plotting total moles adsorbed versus the final equilibrium pressure obtained following each pulse. It might be noted that the time required for an equilibrium pressure to be obtained is influenced by the adsorbent and its pressure.

Typically, one hour was found to be a sufficient length of time for equilibrium to be obtained. Chemisorption uptake is estimated by extrapolating the linear, high pressure, portion of the isotherm to zero pressure and assuming that this intercept represents chemisorption. A sample calculation of gas uptake measurements is presented below and the resulting isotherm presented in Fig. 2.

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Adsorption Isotherm: Sample Calculation

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Catalyst: 3.0% Ru/Al<sub>2</sub>0<sub>3</sub>
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Weight: 1.53 g

Adsorbate: H<sub>2</sub>

Adsorption temperature: 378K

Dosing volume:  $V_1=32.4 \text{ cm}^3$ ,  $T_1=298\text{K}$ 

Adsorption cell: effective volume, V2=21.7 cm<sup>3</sup>, T2=378K

### H<sub>2</sub> Molar Uptake Data

	Pressure (torr)			$H_2$ uptake x $10^5$ (moles)	
,i	Pi	P <sub>expi-1</sub>	Pexpi	ni	ni
1	50.0	0.0	3.0	7.92	7.92
2	54.0	3.0	21.7	3.92	11.8
3	102	21.7	64.8	2,45	14.3
4	176	64.8	132	1.49	15.8
5	300	132	234	2.12	17.9

 $P_i$  = pressure in dising volume prior to admitting to catalyst cell  $P_{exp_i}$  = equilibrium pressure following i aliquot  $n_i$  = molar uptake for the i aliquot(a)

(a) from ideal gas law

$$n_{i} = \frac{P_{i}V_{1}}{RT_{1}} + \frac{P_{exp_{i-1}}V_{2}}{RT_{2}} - \frac{P_{exp_{i}}}{K}$$

$$\kappa = \frac{\kappa^{-1} 1^{T} 2}{v_{1}^{T} 1^{+} v_{2}^{T} 2}$$



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