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THE MECHANISM AND KINETICS OF FISCHER-TROPSCH
SYNTHESIS OVER SUPPORTED RUTHENIUM CATALYSTS

Carl Stephen Kellner
(Ph.D. thesis)

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THE MECHANISM AND KINETICS OF FISCHER-TROPSCH SYNTHESIS
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Ph.D. Thesis

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The Mechanism and Kinetics of Fischer-Tropsch Synthesis
Over Supported Ruthenium Catalysts

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ABSTRACT

A detailed study of the kinetics of the Fischer-Tropsch synthesis of hydrocarbons, methanol, and acetaldehyde, over alumina- and silica-supported ruthenium catalysts has been carried out over a broad range of reaction conditions. Based on these results and information taken from the literature, mechanisms for the formation of normal paraffins, α -olefins, methanol, and acetaldehyde have been proposed.

Rate data were obtained between 448 and 548K, 1 and 10 atm, and H_2/CO ratios between 1 and 3, utilizing a micro flow reactor operated at very low conversions. These conditions allowed the intrinsic reaction kinetics to be observed with minimal interference from secondary reactions. In addition to the studies performed with H_2/CO mixtures, a series of experiments were carried out utilizing D_2/CO mixtures. These studies were used to help identify rate limited steps and steps that were at equilibrium.

A complementary investigation, carried out by in situ infrared spectroscopy, was performed using a Fourier Transform spectrometer. The spectra obtained were used to identify the modes of CO adsorption,

the CO coverage, and the relative reactivity of different forms of adsorbed CO. It was established that CO adsorbs on alumina-supported Ru in, at least, two forms: i) Ru-CO and ii) OC-Ru-CO. Only the first of these forms participates in CO hydrogenation. The coverage of this species is described by a simple Langmuir isotherm.

The kinetics of hydrocarbon synthesis, the olefin to paraffin ratio for each product, and the probability of chain propagation can all be interpreted on the basis of the reaction mechanism described below. Reaction is initiated by the adsorption of CO and its subsequent dissociation. Atomic oxygen is rejected as H_2O and the carbon undergoes stepwise hydrogenation to form CH_x ($x=1-3$) species. Methane is formed by reductive elimination of methyl groups while the formation of higher molecular weight products is initiated by the addition of a CH_2 unit to an adsorbed CH_3 group. Further chain growth then proceeds via a similar process. Olefins are formed by β -elimination of hydrogen from an adsorbed alkyl group and paraffins are formed by reductive elimination of an alkyl group. Rate expressions based on this mechanism are reasonably consistent with the experimental data.

Acetaldehyde, obtained mainly over silica-supported Ru, appears to be formed by a mechanism related to that for hydroformulation of olefins. Following the formation of methyl groups, as discussed above, CO is inserted into the metal-carbon bond of the CH_3 group. The resulting acetyl species then undergoes reductive elimination to produce acetaldehyde. Methanol, rather than acetaldehyde, is observed over alumina-supported Ru. The mechanism by which this product is formed is not clear. However, the observed kinetics are consistent with a

mechanism in which μ -bridge adsorbed CO is hydrogenated to form a methoxy intermediate. Reductive elimination of this moiety results in methanol formation.

The effect of the dispersion of Ru/Al₂O₃ catalysts on their specific activity and selectivity was also investigated. The specific activity for all products decreased rapidly with increasing dispersion; a particularly rapid fall off being observed for dispersions greater than 0.7. The olefin to paraffin ratio of the products and the probability of chain growth were nearly independent of dispersion for dispersions less than 0.6 but decreased sharply at higher dispersions. The origin of the dispersion effects are not fully understood. It may be hypothesized that at least a part of the observed effects is due to changes in the electronic properties of the small Ru particles constituting the catalyst.

CHAPTER I

INTRODUCTION

The Fischer-Tropsch synthesis, a catalytic process by which hydrocarbons and oxygen containing products are produced from carbon monoxide and hydrogen, has attracted a great deal of attention in the last decade. This interest stems largely from the potential of utilizing Fischer-Tropsch synthesis (FTS) to produce transportation fuels and chemical feedstocks from coal. While a very large amount of empirical data (1) have been obtained on catalyst and process performance since the 1920's, when FTS was developed into a viable process (2), only recently have some of the fundamental reactions occurring on the catalyst surface begun to be understood (3,4). Much of what is known about the mechanism of FTS has been obtained through studies of related, homogeneously catalysed, reactions (5,6) but more detailed studies, performed with supported, heterogeneous, catalysts, are still required to develop a clearer understanding of the overall surface chemistry. Development of such information is highly desirable since it could aid in guiding the synthesis of selected products or ranges of products.

Although many of the transition metals will catalyse the reaction between CO and H₂, iron, cobalt, and ruthenium are the most selective for the synthesis of intermediate molecular weight hydrocarbons(1). Of the three, ruthenium has a number of properties that make it particularly attractive as a model catalyst for a fundamental study of FTS. It possesses both high intrinsic activity and selectivity for straight chain product formation and produces few oxygen containing products. It can be reduced readily in flowing hydrogen, is easily supported in

highly dispersed form, and because ruthenium does not form a bulk carbide or oxide under Fischer-Tropsch reaction conditions, as do iron and cobalt, a long induction period is not required prior to the onset of FTS. These properties of ruthenium facilitate the acquisition and interpretation of kinetic data.

The objectives of the present study are to reexamine the kinetics of FTS over supported Ru catalysts, to determine whether these results are compatible with the current understanding of the mechanisms of FTS, and, when possible, to discriminate between plausible, parallel, reaction pathways. To this end, the kinetics of C_1 through C_{10} paraffin and olefin formation have been determined, over Ru/Al_2O_3 and Ru/SiO_2 catalysts, over a broad range of realistic Fischer-Tropsch reaction conditions. The pressure has been varied from 1 to 10 atm, the temperature from 448 to 548K, and the H_2/CO ratio from 1 to 3. However, rather than operating at the high conversions typical of an industrial process, conversions have been kept below 2% in order that the intrinsic kinetics could be observed. The kinetics of methanol and acetaldehyde formation, the most abundant organic oxygen containing products observed over Ru/Al_2O_3 and Ru/SiO_2 catalysts, respectively, have also been investigated.

Because kinetic data alone is rarely capable of discriminating between similar reaction mechanisms (4), additional information has been obtained by in situ infrared spectroscopy of the catalyst during reaction and by carrying out a series of runs using D_2/CO rather than H_2/CO mixtures. In situ infrared spectroscopic studies allow the types of adsorbed species present on the catalyst surface to be determined

(7) and, in addition, provides a method by which changes in the concentrations of these species with reaction conditions or time can be observed. Various types of experiments can be carried out with isotopically labeled reactants (8). In the present study the focus has been on determining how using D_2/CO in the place of H_2/CO mixtures effects the observed reaction rates. From such information, conclusions can be drawn concerning the nature of elementary steps involving the transfer of hydrogen atoms.

The influence of Ru dispersion on catalyst activity and selectivity has also been investigated as part of this effort. Previous studies have demonstrated that metal dispersion can have an effect on catalyst activity and selectivity (9). The purpose of these studies is to establish the extent to which dispersions can be used to alter the distribution of products obtained.

The balance of this thesis is divided into five parts, reflecting individual efforts undertaken in the course of this work. A review of the literature pertaining to each effort is presented at the beginning of each chapter. Chapter II deals with the interpretation of H_2/D_2 isotope effects observed during the synthesis of methane and higher molecular weight hydrocarbons. The results of in situ infrared studies are discussed in Chapter III. Determination of the kinetics of hydrocarbon synthesis is discussed in Chapter IV and the experimental data are compared with rate and product distribution expressions derived on the basis of a proposed mechanism. In Chapter V observations of methanol and acetaldehyde synthesis are discussed in the light of mechanisms for the formation of these products. Finally, Chapter VI deals

with the effect of the dispersion of Ru/Al₂O₃ on the activity and selectivity of these catalysts. Several appendices dealing with experimental apparatus and procedures appear at the end of the thesis.

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CHAPTER II

Evidence For H_2/D_2 Isotope Effects on
Fischer-Tropsch Synthesis Over Supported
Ruthenium Catalysts

ABSTRACT

The effects of using D_2 rather than H_2 during Fischer-Tropsch synthesis were investigated using alumina- and silica-supported Ru catalysts. For the alumina-supported catalysts, the rate of CD_4 formation was 1.4 to 1.6 times faster than the formation of CH_4 . A noticeable isotope effect was also observed for higher molecular weight products. The magnitude of the isotope effects observed using the silica-supported catalyst was much smaller than that found using the alumina-supported catalysts. The formation of olefins relative to paraffins was found to be higher when H_2 rather than D_2 was used; independent of the catalyst support. The observed isotope effects are explained in terms of a mechanism for CO hydrogenation, and are shown to arise from a complex combination of the kinetic and equilibrium isotope effects associated with elementary processes occurring on the catalyst surface.

INTRODUCTION

Results from a number of recent studies (1-13) suggest that the catalytic synthesis of CH_4 from CO and H_2 over group VIII metals proceeds via stepwise hydrogenation of atomic carbon, formed upon dissociation of chemisorbed CO. It has also been proposed that the formation of higher molecular weight hydrocarbons is initiated by the addition of a methyl group to a methylene group and that further chain growth occurs by the reaction of methylene groups with adsorbed alkyl groups (14, 15). The alkyl groups then react to form olefins and paraffins via either hydrogen elimination or addition. Consistent with these views of CO hydrogenation, one would expect to observe an isotopic effect if D_2 were used instead of H_2 . While several attempts have been made to observe such an effect, the results available thus far have been contradictory. In early studies by Jungers et al. (16, 17), the hydrogenation of CO to CH_4 over Ni was observed to proceed more rapidly with D_2 than H_2 and the activation energy was lower for D_2 . Recent studies by Mori et al. (18) have confirmed this observation and indicate that methanation over Ni is 1.4 times faster with D_2 than with H_2 . Sakharov and Dokukina (19) also observed an inverse isotope effect for a $\text{Co/ThO}_2/\text{Kieselguhr}$ catalyst. For temperatures between 449 and 466K they found that the formation of CD_4 was 1.2 to 1.5 times faster than the formation of CH_4 . A normal isotope effect was observed by McKee (20) for CH_4 synthesis over Ru powder. The ratio of CH_4 to CD_4 formation was 2.2 over the temperature range of 298 to 423K. In contrast to these results, Dalla Betta and Shelef (20,21) reported that no isotopic effect could be discerned for either CH_4 or

total hydrocarbon formation over Ni/ZrO_2 , $\text{Ru/Al}_2\text{O}_3$, or $\text{Pt/Al}_2\text{O}_3$ for temperatures between 423 and 498K. Based on this evidence it was suggested that CO dissociation is likely to be the rate-determining step in CO hydrogenation. In a comment on these results, Wilson (23) noted that the overall isotope effect could arise from a combination of kinetic and equilibrium isotope effects, the former favoring the reaction of H_2 and the latter favoring the reaction of D_2 . As a result of this, he concluded that the presence or absence of an isotope effect cannot be used to identify the rate determining step.

The present study was undertaken to reexamine the nature of the H_2/D_2 isotope effect associated with the synthesis of CH_4 and higher molecular weight hydrocarbons over silica- and alumina-supported Ru. These investigations were carried out at 1 and 10 atm in the temperature interval of 453 to 548K. An inverse isotope effect was observed for the alumina-supported catalysts, which was largest for CH_4 and declined with increasing carbon number. The magnitude of the inverse isotope effect observed using the silica-supported catalyst was much smaller, and a normal isotope effect was observed for some of the products. A small normal isotope effect on the olefin to paraffin ratio was observed over both catalysts. The significance of these observations is discussed in the light of a proposed mechanism for the hydrogenation of CO over Ru.

EXPERIMENTAL

Catalysts

Two alumina-supported catalysts and one silica-supported catalyst were prepared using Kaiser KA-201 γ -alumina and Davison 70 silica gel as the supports. A 3.0% Ru/ Al_2O_3 and a 1.2% Ru/ SiO_2 catalyst were prepared by incipient wetness impregnation of the support with an aqueous solution of RuCl_3 , acidified to pH = 2 to suppress hydrolysis. The resulting slurry was air-dried, and then heated slowly in vacuum from 298 to 423K. Reduction of the chloride was carried out in flowing H_2 . The temperature was raised slowly from 298 to 673K and then maintained at 673K for 8 hr.

A second alumina-supported catalyst was prepared by adsorption of $\text{Ru}_6\text{C}(\text{CO})_{17}$ from a pentane solution under oxygen and moisture free conditions. Synthesis of the cluster complex and details of the impregnation procedure have been described previously (24). Once dried this catalyst, designated as 1.0% $\text{Ru}_6/\text{Al}_2\text{O}_3$, was reduced in flowing H_2 under conditions identical to those used to reduce the catalysts prepared from RuCl_3 .

The dispersion of the 1.0% $\text{Ru}_6/\text{Al}_2\text{O}_3$ and the 3.0% Ru/ Al_2O_3 catalysts, measured by H_2 chemisorption, were found to be 1.0 and 0.5, respectively. The dispersion of the 1.2% Ru/ SiO_2 catalyst could not be determined by this technique since a reproducible determination of H_2 uptake could not be obtained. 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 validity of this assumption is supported by previous

studies with low dispersion $\text{Ru}/\text{Al}_2\text{O}_3$ catalysts (25) and by the observation that infrared spectra of CO adsorbed on the Ru/SiO_2 used in this study (7,26) show only a single band, attributable to linearly adsorbed CO.

All reactions were carried out using a premixed feed composed of H_2 or D_2 and CO at a ratio of $\text{H}_2(\text{D}_2)/\text{CO} = 3.0$. The feed mixtures were blended in small cylinders using pure components. Following filling, the bottom of the cylinder containing the mixture was heated for one day to assure uniform gas mixing. The blended mixture was then analyzed by gas chromatography to establish the concentration of CO. If the original mixture was not correct, additional CO or H_2 (D_2) was added. By following this procedure, it was possible to obtain mixtures containing $25 \pm 0.5\%$ CO.

Procedure

Rate data were obtained using a stainless steel microreactor heated in a fluidized bed. The reaction products were analyzed using an on-line gas chromatograph fitted with balanced 2.4 mm by 1 m columns packed with Chromosorb 106. The column oven was temperature programmed from 318 to 503K at 10K/min, and the hydrocarbon products were detected by a flame ionization detector. Calibration of the chromatograph was carried out using mixtures containing known concentrations of the products. In addition, by injecting pure samples of CH_4 and CD_4 it was established that the detector sensitivities for deuterated and hydrogenated products were identical.

Each experiment with a fresh catalyst charge [30 mg for the 3.0% $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst and 100 mg for the 1.0% $\text{Ru}_6/\text{Al}_2\text{O}_3$ and the 1.2%

Ru/SiO₂ catalysts was initiated by a 10 to 12 hr reduction in flowing H₂ at 673K and 10 atm. The temperature was then lowered to 498K and the feed mixture was introduced at a flow rate of 200 cm³/min (NTP). Ten minutes after the reaction began, a gas sample was taken for analysis and the gas feed was switched over to pure H₂ 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

Arrhenius plots for the rates of formation of C₁ through C₅ hydrocarbons over Ru₆/Al₂O₃ and Ru/SiO₂ are given in Figs. 1-5. The open points represent turnover numbers measured with H₂ and the solid points represent turnover numbers measured with D₂. The rates of formation of C₂ through C₄ paraffins and olefins have been shown separately in Figs. 2-4. Representation in this fashion was not possible, though, for the C₅ products since the resolution of the chromatographic peaks for olefins and paraffins was inadequate.

The data presented in Fig. 1 show that the production of CD₄ occurs approximately 1.5 times faster than CH₄ over Ru₆/Al₂O₃, both at 1 and 10 atm. At 10 atm the production of CD₄ is also favored over

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XBL 807-10808

Fig. 1. Arrhenius plots for the formation of methane at 1 and 10 atm.

Ru/SiO_2 , but the magnitude of the inverse isotope effect is now 1.1. When the pressure is reduced to 1 atm, no isotope effect can be detected for this catalyst. It is noted further that the activation energy for both CH_4 and CD_4 lies between 27 and 28 Kcal/mole, independent of the total pressure or catalyst composition.

Figures 2-5 show that an inverse isotope effect is also apparent for the production of C_2 through C_5 olefins and paraffins over the alumina-supported catalyst. The upward curvature of the Arrhenius plots for C_2D_6 and C_2H_6 can be explained in the following manner. For temperatures below about 493K, olefins and paraffins are produced by parallel processes as suggested by the fact that the feed flow rate does not alter the olefin to paraffin ratio of the products. At higher temperatures, hydrogenation of the olefin takes place. The presence of this secondary reaction is confirmed by observing an increase in the olefin to paraffin ratio with increasing feed flow rate. When partial hydrogenation of the olefin product does occur, the Arrhenius plot curves upwards, since the paraffin is now produced via two pathways.

Examination of the Arrhenius plots for C_2 through C_5 products formed over the Ru/SiO_2 catalyst show that the isotope effects are significantly different from those observed using the alumina-supported catalyst. Normal isotope effects are seen for the C_2 and C_4 products but no significant isotope effect is found for the C_3 or C_5 products. Here again, the upwards curvature in the Arrhenius plots for the C_2 through C_4 paraffins at higher temperatures can be ascribed to partial hydrogenation of the corresponding olefins.

Fig. 2. Arrhenius plots for the formation of ethylene and ethane at 10 atm.

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Fig. 3. Arrhenius plots for the formation of propylene and propane at 10 atm.

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Fig. 4. Arrhenius plots for the formation of butene and butane at 10 atm.

Fig. 5. Arrhenius plots for the formation of pentene and pentane at 10 atm.

Experiments identical to those shown in Figs. 2-5 were also carried out at 1 atm. The isotope effects for the alumina-supported catalyst were similar to those observed at 10 atm. Virtually no isotope effect was observed, though, for the silica-supported catalyst.

To determine whether the manner of preparation of the alumina-supported catalyst altered the nature or magnitude of the isotope effect, experiments were conducted with the $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst prepared by reduction of RuCl_3 . A comparison of the isotope effects for C_1 through C_5 hydrocarbons observed over the catalysts prepared from $\text{Ru}_6\text{C}(\text{CO})_{17}$ and RuCl_3 is given in Table I. It is seen that the isotope effects are virtually the same for the two catalysts. As a consequence, it seems appropriate to ascribe the observed isotope effects to the nature of the interactions between ruthenium and alumina rather than to the origin of the ruthenium.

The results presented in Table I indicate further that the magnitude of the isotope effect declines as the number of carbon atoms in the product increases. This trend is shown even more clearly in Fig. 6. Quite interestingly, for $n > 5$ the isotope effect becomes less than unity, indicating a slightly faster product formation rate with H_2 than with D_2 .

The effects of temperature on the olefin to paraffin ratio are shown in Figs. 7-9. For each catalyst, the ratio is observed to pass through a maximum with increasing temperature. The position of the maximum defines the temperature above which hydrogenation of the olefin becomes significant. For all three products the olefin to paraffin ratio is higher when the silica-supported catalyst is used, but the

Table I. Comparison of the H_2/D_2 Isotope Effects for 1.0% Ru_6/Al_2O_3 and 3.0% Ru/Al_2O_3 .

	455K		475K		500K	
	Ru_6/Al_2O_3	Ru/Al_2O_3	Ru_6/Al_2O_3	Ru/Al_2O_3	Ru_6/Al_2O_3	Ru/Al_2O_3
$N_{C_1}^D / N_{C_1}^H$	1.57	1.61	1.49	1.56	1.40	1.52
$N_{C_2}^D / N_{C_2}^H$	1.22	1.18	1.19	1.16	1.16	1.14
$N_{C_3}^D / N_{C_3}^H$	1.17	1.19	1.19	1.21	1.23	1.22
$N_{C_4}^D / N_{C_4}^H$	1.08	1.08	1.12	1.13	1.15	1.18
$N_{C_5}^D / N_{C_5}^H$	1.05	1.05	1.07	1.08	1.12	1.12

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Fig. 6. Dependence of the isotope effect on the number of carbon atoms in the product.

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Fig. 7. Dependence of the olefin to paraffin ratio for C_2 products on the inverse temperature.

XBL 807-10815

Fig. 8. Dependence of the olefin to paraffin ratio for C₃ products on the inverse temperature.

XBL 807-10816

Fig. 9 Dependence of the olefin to paraffin ratio for C_4 products on the inverse temperature.

temperature at which olefin hydrogenation becomes significant is higher for the alumina-supported catalyst. While the use of D_2 instead of H_2 does not influence the general characteristics of the olefin to paraffin ratio dependence on temperature, a number of subtle effects are apparent. For the alumina-supported catalyst, there is virtually no isotope effect on the olefin to paraffin ratios for C_2 and C_4 products. However, the ratio of propylene to propane is definitely higher when H_2 rather than D_2 is present in the feed. For the silica-supported catalyst, no isotope effect is detectable for the C_2 products at temperatures below 500K. Above this temperature, though, the ethylene to ethane ratio is higher in the presence of D_2 . By contrast, the olefin to paraffin ratios for the C_3 and C_4 products are higher in the presence of H_2 over the whole temperature range. The olefin to paraffin ratio was also examined for the data obtained at 1 atm. In this case the olefin to paraffin ratios were approximately three fold higher than those shown in Figs. 7-9 and higher values were obtained with H_2 than with D_2 for all three products over both catalyst.

DISCUSSION

The data presented here clearly show that an inverse isotope effect can be observed for the formation of CH_4 over Ru catalysts. The magnitude of the effect is 1.6-1.4 for the alumina-supported catalysts, both at 1 and 10 atm. For silica-supported Ru the effect is 1.1 at 10 atm but drops to 1.0 at 1 atm. These results contradict the conclusion of Dalla Betta and Shelef (21) that there is no isotope effect for methane formation over Ru. Since the weight loading and dispersion of the catalyst used by Dalla Betta and Shelef were similar to that of the

$\text{Ru}_6/\text{Al}_2\text{O}_3$ catalyst used in this work, it is difficult to understand why these authors did not observe an isotope effect. One possibility may be that an insufficient amount of data were taken, particularly with D_2 . The present results also differ from those obtained by McKee (20). It should be noted, though, that comparison in this case may not be appropriate since McKee's studies were conducted with Ru powder at much lower pressures (60 Torr CO and 60 Torr H_2) and temperatures (298 to 423K) than those used here. Furthermore, as was noted by Dalla Betta and Shelef (21), the analytical procedure used by McKee may not have been free of error. Products were detected by a mass spectrometer connected to the reaction chamber by a molecular leak. Since this method of sampling can give rise to different sensitivities for CH_4 and CD_4 , and since calibration of the mass spectrometer was not discussed, it is not possible to know whether the reported results are accurate.

An interpretation of the isotope effects observed in the present study can be developed by consideration of the following reaction network:

This mechanism is supported by a significant number of recent investigations (1-15) and has been discussed in detail by Bell (27). As a result, no attempts will be made here to justify the elementary steps included.

Overall rate expressions for the formation of methane can be derived from the proposed scheme provided a number of simplifying assumptions are invoked. The first is that the Ru surface is nearly saturated by adsorbed CO. This assumption is supported by in situ infrared observations carried out both at low and high pressure (7,26,28,29). The second assumption is that water is the primary product through which oxygen is removed from the catalyst surface. Here, too, the assumption is substantiated by experimental evidence (7,26). The third assumption is that all of the steps indicated as being reversible are, in fact, at equilibrium. No substantiation of this assumption is currently possible.

Two limiting forms can be obtained for the kinetics of methane formation, depending upon whether methanation or the synthesis of higher molecular weight hydrocarbons is dominant (26,27). In the former case, the rate of methane formation is given by

$$N_{C_1} = k_e P_{H_2}^{1.5} / P_{CO} \quad (1)$$

$$k_e = \frac{K_3}{K_1} (k_4 k_8 K_5 K_6 K_7)^{1/2} \quad (2)$$

where k_i and K_i are the rate coefficient and equilibrium constant, respectively, for the i^{th} elementary reaction. In the latter case, the rate is given by

$$N_{C_1} = k_e P_{H_2}^{1.5} / P_{CO}^{1.33} \quad (3)$$

$$k_e = k_8 \left[\frac{k_4 K_2 K_3^{3.5} K_5 K_6 K_7^2 (1-\alpha)}{k_p K_1^4} \right]^{1/3} \quad (4)$$

where k_p is the rate coefficient for the addition of CH_2 groups to adsorbed alkyls (i.e. reactions 9, 12, etc.) and α is the probability of chain propagation (30). With the exception of studies conducted at pressures of 1 atm or less, using H_2 to CO ratios greater than three, neither of the limiting assumptions is strictly valid. However, recent experimental studies by Kellner and Bell (26) have shown that for pressures between 1 and 10 atm and H_2/CO ratios between 1 and 3 the kinetics of methane formation can be described empirically by the expression $N_{C_1} = k_e P_{H_2}^{1.4} / P_{CO}$, in good agreement with Eqn. 1.

The forms of Eqns. 1 and 3 indicate that the effective rate coefficient for methane synthesis is a complex product of rate coefficients and equilibrium constants. As a consequence, the observed

isotope effect must result from the combination of kinetic and equilibrium isotope effects, as suggested by Wilson (23). To further pursue the influence of these two effects, it is useful to recall that rate coefficients and equilibrium constants can be expressed in the formalism of statistical mechanics (31). Thus,

$$K = \frac{kT}{h} \frac{q^\ddagger}{\prod_i q_r^{v_i}} \quad (5)$$

$$K = \frac{\prod_j q_p^{v_j}}{\prod_i q_r^{v_i}} \quad (6)$$

where (kT/h) is a frequency factor; q_r , q_p , and $q^\ddagger$ are the partition functions for reactants, products, and transition state complexes; and v_i and v_j are the stoichiometric coefficients for reactant i and product j . Changes in the magnitudes of k and K due to isotopic substitution result from the influences of molecular mass on the molecular partition functions. In most instances, the largest portion of the isotope effect arises from changes in the ground state vibrational frequencies.

Ozaki (32) has noted that the differences in the ground state vibrational frequencies of deuterated and hydrogenated species usually lead to the conclusion that the equilibrium constant for addition of deuterium to an adsorbed species is larger than that for the addition of hydrogen. An example of this generalization which is relevant to the present discussion has been reported recently by Calvert et al. (33). In this work it was shown that deuterium is preferentially in-

incorporated into methyl and methylene ligands present in triosmium complexes. The equilibrium constant for the reaction $\text{Os}_3(\text{CO})_{10}\text{CH}_2\text{D}_2 \rightleftharpoons \text{Os}_3(\text{CO})_{10}\text{CD}_2\text{H}_2$ was determined to be 2.50 and that for the reaction $\text{Os}_3(\text{CO})_{10}(\text{CH}_2\text{D})\text{D} \rightleftharpoons \text{Os}_3(\text{CO})_{10}(\text{CD}_2\text{H})\text{H}$ was found to be 1.74. Based on this evidence, one would suspect that the product $K_5K_6K_7$, appearing in Eqns. 1 and 3, should be significantly larger when D_2 is involved in steps 5 through 7 rather than H_2 .

The equilibrium isotope effect for $\text{H}_2(\text{D}_2)$ chemisorption, reaction 3, can be examined explicitly. If it is assumed that the adsorbed atoms are immobile but have three degrees of vibrational freedom, then it can readily be shown that

$$\frac{K_3^{\text{D}}}{K_3^{\text{H}}} = \left(\frac{m_{\text{H}_2}}{m_{\text{D}_2}} \right)^{5/2} \exp \left\{ \left[-2 \sum_{i=1}^3 (\nu_i^{\text{D}} - \nu_i^{\text{H}}) + (\nu_1^{\text{D}_2} - \nu_1^{\text{H}_2}) \right] \frac{h}{2kT} \right\} \quad (7)$$

where m_{H_2} and m_{D_2} are the masses of H_2 and D_2 , ν_i^{H} and ν_i^{D} are the vibrational frequencies for adsorbed H and D atoms, and $\nu_1^{\text{H}_2}$ and $\nu_1^{\text{D}_2}$ are the vibrational frequencies for gaseous H_2 and D_2 . Evaluation of $K_3^{\text{D}}/K_3^{\text{H}}$ using the values of the vibrational frequencies given in Table II shows that this ratio lies between 0.79 and 0.62 for temperatures between 453 and 543K. It is significant to note that while $K_3^{\text{D}}/K_3^{\text{H}} < 1$ over the temperature range of interest in these studies, the argument of the exponential factor in Eqn. 7 leads to the expectation that the heat of adsorption for D_2 on Ru should be 1.34 Kcal/mole larger than that for H_2 .

These conclusions are consistent with experimental observations on Ni.

Table II. Vibrational Frequencies for Molecular and Atomically Adsorbed H_2 and D_2 .

<u>Species</u>	<u>Mode</u>	<u>Frequency (cm⁻¹) (a)</u>
H_2	ν (H-H)	4161
D_2	ν (D-D)	2993
M-H	ν (M-H)	2250-1700
	δ (M-H) (b)	800-600
M-D	ν (M-D)	1591-1202
	δ (M-D) (b)	566-424

(a) Taken from ref. (35)

(b) Doubly degenerate

By means of calorimetric measurements on a Ni film, Wedler et al. (34) determined that the heat of adsorption of D_2 was about 1 Kcal/mole larger than that for H_2 . The displacement of adsorbed H atoms by D_2 and of adsorbed D atoms by H_2 on Ni catalysts was investigated by Gundry (35). His results showed that the apparent equilibrium constant for displacement, which is equivalent to K_3^D/K_3^H , varied from 2.4 at 178K to near unity at 273K. Based on this variation with temperature, it was estimated that the heat of adsorption of D_2 was 0.60 Kcal/mole greater than that for H_2 . The stronger adsorption of D_2 has also been confirmed by Wedler and Stanelmann (36) on a Ni film. Extrapolation of Gundry's results to the temperature levels used in this study would also lead to the conclusion that $K_3^D/K_3^H < 1$.

The kinetic isotope effect for reactions involving the addition of hydrogen has also been considered by Ozaki (32). Here again, he concludes that differences in the vibrational frequencies of deuterated and hydrogenated species are the primary origin of the effect and that in most cases $k_H > k_D$. For reactions involving a molecule of H_2 or D_2 , and an adsorbed species (i.e., reaction 4), the ratio of masses arising from the transitional and rotational portions of the partition functions of H_2 and D_2 only serve to further increase the magnitude of the kinetic isotope effect.

Based upon the factors just considered, it is clear that the overall isotope effect on methane formation results from a complex combination of kinetic and equilibrium effects. Since the magnitude of these individual effects cannot be predicted reliably, it is not possible

to conclude whether the observed isotope effect is consistent with the structure of the effective rate coefficient appearing in Eqns. 1 and 3. What is evident, though, is that small changes in the isotope effects associated with individual elementary processes will alter the overall isotope effect. Such changes could arise from modifications of the metal dispersion and/or interaction with the support and might explain why the isotope effect is substantially smaller for the silica-supported catalyst than for either of the alumina-supported catalysts.

The data presented in Fig. 6, show that the magnitude of the inverse isotope effect decreases with increasing carbon number. This pattern can be understood in the following fashion. If it is assumed that the probability of chain propagation, α , is independent of chain length, n , then the rate of formation of hydrocarbons containing n atoms can be expressed as

$$N_{C_n} = (k_{to} \theta_v + k_{tp} \theta_H) \alpha^{n-1} \theta_{CH_3} \quad (8)$$

$$= (1 + \frac{k_{to} \theta_v}{k_{tp} \theta_H}) \alpha^{n-1} k_{tp} \theta_H \theta_{CH_3} \quad (9)$$

where k_{to} and k_{tp} are the rate coefficients for termination of chain growth by formation of olefins and paraffins (i.e. reactions 10 and 11), θ_v is the fraction of the catalyst surface that is vacant, and θ_H and θ_{CH_3} are the fractions of the surface covered by H atoms and CH_3 groups. The second term in the parenthesis of Eqn. 9 can be rewritten as

$$\frac{k_{to}^{\theta}}{k_{tp}^{\theta}} = \frac{k_{to}}{k_{tp}^{\frac{1}{2}} K_3^{\frac{1}{2}} P_{H_2}^{\frac{1}{2}}} \quad (10)$$

$$= \beta / P_{H_2}^{\frac{1}{2}} \quad (11)$$

The magnitude of the isotope effect for any value of n can now be expressed by taking the ratio of the rate in the presence of D_2 , $N_{C_n}^D$, to that in the presence of H_2 , $N_{C_n}^H$. Combining Eqns 9 and 11 with the expression $N_{C_1} = k_8^{\theta} H^{\theta} CH_3$, we obtain.

$$\frac{N_{C_n}^D}{N_{C_n}^H} = \frac{k_{tp}^D}{k_{tp}^H} \frac{k_8^H}{k_8^D} \frac{(1 + \beta^{D/P_{D_2}})^{\frac{1}{2}}}{(1 + \beta^{H/P_{H_2}})^{\frac{1}{2}}} \left(\frac{\alpha^D}{\alpha^H} \right)^{n-1} \frac{N_{C_1}^D}{N_{C_1}^H} \quad (12)$$

The form of Eqn. 12 suggests that the isotope effect for any carbon number can be related to that observed for methane. To account for the decrease in $N_{C_n}^D / N_{C_n}^H$ with n , it must be concluded that $\alpha^D < \alpha^H$. It is also noted that Eqn. 12 predicts that for a sufficiently large value of n , $N_{C_n}^D / N_{C_n}^H$ could become less than one. While there is considerable amount of scatter in the data for $n > 5$ shown in Fig. 6, it does appear that the isotope effect eventually becomes smaller than unity.

The influence of H_2 and D_2 on the olefin to paraffin ratio can also be understood in the context of the present discussion. The proposed reaction mechanism leads to the following expression for the olefin to paraffin ratio:

$$\frac{N_{C_n}^D}{N_{C_n}^H} = \frac{k_{to}}{k_{tp} K_3^{1/2} P_{H_2}^{1/2}} \quad (13)$$

$$= \beta / P_{H_2}^{1/2}$$

This expression is found to be in good agreement with experimental data taken by Kellner and Bell (26) for temperatures below which olefin hydrogenation is not significant. The form of Eqn. 13 again indicates that both kinetic and equilibrium isotope effects will influence the olefin to paraffin ratio. Since it has already been shown that

$K_3^D < K_3^H$, the observation of a normal isotope effect on the olefin to paraffin ratio implies that $(k_{to}^D / k_{tp}^D) < (k_{to}^H / k_{tp}^H)$ or alternatively that $(k_{tp}^D / k_{to}^D) > (k_{tp}^H / k_{to}^H)$.

CONCLUSIONS

The results of the present investigation have shown that an inverse isotope effect can be observed during the synthesis of CH_4 over silica- and alumina-supported Ru catalysts, and that the magnitude of the effect is larger for alumina-supported catalysts.

Noticeable isotope effects have also been observed during the synthesis of C_2 through C_{11} olefins and paraffins. For C_2 through C_5 hydrocarbons, synthesis over an alumina-supported catalyst occurs more rapidly in the presence of D_2 rather than H_2 , but the magnitude of the inverse isotope effect declines towards unity with increasing number of carbon atoms in the product. The synthesis of C_6 through C_{11} hy-

drocarbons appears to be favored by H_2 , and, thus, a normal isotope effect is observed for these products.

The olefin to paraffin ratio of the products also depends on whether D_2 or H_2 is the reactant. Olefin formation is favored with H_2 over both silica- and alumina-supported catalysts.

The observed isotope effects can be rationalized on the basis of a mechanism proposed to describe the formation of CH_4 and higher molecular weight products. Rate expressions derived from this mechanism lead to the conclusion that the overall isotope effect results from a combination of the kinetic and equilibrium isotope effects associated with individual elementary steps. The proposed mechanism also provides explanations for the decline in the magnitude of the inverse isotope effect with increasing product carbon number and the higher olefin to paraffin ratio observed when using H_2 .

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Infrared Studies of Carbon Monoxide Hydrogenation Over
Alumina-Supported Ruthenium

ABSTRACT

The nature of the species present on a Ru/Al₂O₃ catalyst during CO hydrogenation was studied by means of Fourier transform infrared spectroscopy. Three forms of adsorbed CO were identified, designated as linearly-adsorbed, diadsorbed, and μ -bridge adsorbed. The coverage by the linearly-adsorbed form of CO obey a Langmuir isotherm under reaction conditions. The equilibrium constant associated with this isotherm is given by $K_{CO} = 1.1 \times 10^{-9} \exp (25,000/RT) \text{ atm}^{-1}$. The di-adsorbed species is associated with individual Ru atoms and clusters and, in contrast to linearly-adsorbed CO, does not readily undergo hydrogenation at temperatures below 548K. The μ -bridge form of adsorbed CO may involve either a pair of Ru sites or a Ru site and an adjacent Lewis acid site. Hydrocarbon, formate, and carbonate structures were also observed in the course of this study. It was established, however, that these species are present on the alumina support and are not intermediates of CO hydrogenation over Ru.

INTRODUCTION

Infrared spectra taken during the hydrogenation of CO over ruthenium catalysts have helped to identify the dominant species adsorbed on the catalyst (1-5). Dalla Betta and Shelef (1) have reported that the surface of a Ru/Al₂O₃ catalyst is nearly saturated by adsorbed CO at temperatures up to 523K. It was suggested that the presence of hydrogen on the catalyst surface weakens the C-O bond of chemisorbed CO, since the band for this species appeared at a lower frequency than that observed for CO chemisorbed in the absence of hydrogen. At higher temperatures the build up of carbon on the catalyst caused a further shift of the CO bond to lower frequencies and a decrease in the band intensity. Bands attributable to hydrocarbon, formate, and carbonate structures were also observed but these species were ascribed to reaction products adsorbed on the support. Chemisorbed CO has also been observed as a dominant species in the studies conducted by Ekerdt and Bell (2,3) using a Ru/SiO₂ catalyst. In this work the position and intensity of the CO band were found to be independent of the H₂/CO ratio or the CO partial pressure. A decrease in the band intensity, unaccompanied by a shift in position, was observed with increasing temperature and was ascribed to a reduction in the CO coverage. Bands were also observed for hydrocarbon species. These structures could be removed from the catalyst surface by hydrogenation, but did not appear to be intermediates in the synthesis of stable products. Additional observations concerning the hydrocarbon structures formed on Ru/SiO₂ and Ru/Al₂O₃ catalysts have been presented by King (4,5). Strong bands attributable to long-chain saturated hydrocarbons were observed at temperatures below

473K. While the exact point of attachment of these structures could not be defined, it was concluded that the species observed were not intermediates in the formation of gas phase products. At higher temperatures, changes in the shape and position of the hydrocarbon band suggested the presence of short-chain species. It was proposed that these species are attached to the metal surface and might be intermediates in the synthesis reaction.

The primary objective of the present investigation was to characterize more fully the influence of reaction and concentration of the species adsorbed on a $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst during CO hydrogenation. Fourier transform infrared spectroscopy was used for this purpose, and particular attention was devoted to interpretation of the bands ascribed to chemisorbed CO. Working under conditions chosen to avoid significant catalyst deactivation, three different forms of adsorbed CO were identified. These are designated as linearly-adsorbed, di-adsorbed, and μ -bridge adsorbed CO. A detailed study was made of the effects of reaction conditions on the position and intensity of the band associated with the linearly-adsorbed CO. Based on these observations, estimates were made of the variation in the coverage by this species with CO partial pressure and catalyst temperature. As a complement to these studies the kinetics of forming C_1 through C_{10} hydrocarbons were examined in detail. The results of these efforts together with a discussion of the mechanism of hydrocarbon synthesis over ruthenium will be presented separately (6).

EXPERIMENTAL

The 1% Ru/Al₂O₃ catalyst used for these studies was prepared by adsorption of the Ru₆C(CO)₁₇ from pentane solution onto Kaiser KA-201 alumina. Details concerning synthesis of the complex, impregnation of the support and the reduction of the final catalyst are described in references (6,7). A 75 mg portion of the reduced catalyst was pressed into a 20 mm by 0.25 mm disk and placed inside a small infrared reactor (8).

Prior to each series of experiments, the catalyst was reduced in flowing H₂ for 10 to 12 hours at 673K and 10 atm. The temperature was then lowered to 498K and a premixed feed, containing H₂ and CO, was introduced at a flow rate of 200 cm³/min (NTP). Ten minutes after reaction had begun, the effluent gas was analyzed by gas chromatography (6), and the gas feed was switched over to pure H₂ for 1 hour. By alternating short reaction periods and longer reduction periods, a stable catalyst activity could be achieved after several cycles. This procedure also eliminated the build up of large amounts of carbon and the concurrent deactivation of the catalyst. Once a stable catalyst activity had been obtained, reaction conditions were adjusted to those desired for a particular experiment.

Infrared spectra were taken with a Digilab FTS-10M Fourier transform infrared spectrometer, using a resolution of 4 cm⁻¹. For the observation of steady state phenomena, 100 interferograms, each acquired in about 1.25 s, were co-added to improve the signal to noise ratio. However, good spectra could also be obtained by co-adding as few as 10 interferograms. 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 disk, placed downstream from a catalyst disk, during reaction. The latter two spectra were used to subtract out infrared adsorptions due to the support and the gas phase.

RESULTS AND DISCUSSION

Infrared spectra of the catalyst taken under reaction conditions showed bands in two regions, one set appearing between 3200 and 2400 cm^{-1} and another set appearing between 2300 and 1200 cm^{-1} . The bands in the first of these regions are associated with adsorbed hydrocarbons, while bands in the second region are due to carbonyl, carbonate, and formate structures. To identify whether these structures are present on the surface of the metal and/or support and to identify the relative stability and reactivity of individual structures, spectra were taken under a variety of conditions.

Bands Observed Between 2300 and 1200 cm^{-1}

Spectral Observations - Representative spectra of the most prominent features observed in this region, during reaction at pressures of 1, 5, and 10 atm, are shown in Fig. 1a. The spectrum shown at each pressure represent the difference in the adsorbances of the catalyst and reference disks, measured in the presence of the same gas composition. A broad band can be seen near 2000 cm^{-1} superimposed on which is a weakly defined shoulder of 2040 cm^{-1} and a partially resolved band at 1960 cm^{-1} . All three features appear immediately upon passage of the H_2 -CO mixture over the catalyst and the integrated intensity of the band envelope grows by about 10-15% over a 20 minute period of

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Fig. 1. Spectra obtained at 548K during reaction and subsequent reduction in H₂: (a1) P = 10 atm, H₂/CO = 2; (a2) P = 5 atm, H₂/CO = 2; (a3) P = 1 atm, H₂/CO = 2; (b1) after (a1) and following reduction in H₂ at 10 atm; (b2) after (a2) and following reduction in H₂ at 5 atm; (b3) after (a3) and following reduction in H₂ at 1 atm; (c1) difference between (a1) and (b1); (c2) difference between (a2) and (b2); (c3) difference between (a3) and (b3).

observation. It is significant to note, though, that the positions of the three bands are totally unaltered during this period. Figure 1b shows spectra taken following cessation of the reaction and reduction in H_2 . The intense band near 2000 cm^{-1} is now completely eliminated, thereby revealing very clearly the bands at 2040 and 1960 cm^{-1} . It is noted that the intensities of these two peaks are independent of the reaction pressure. Moreover, the structures giving rise to these features are stable to reduction at temperatures below 548K and can only be removed at higher temperatures. Spectra of the species removed by reduction at reaction temperatures are shown in Fig. 1c, and are obtained by taking the difference between the spectra presented in Figs. 1a and 1b. Each spectrum consists of a broad, asymmetric band which does not return to the baseline at low frequencies. With increasing reaction pressure, the intensity of this band increases and the band maximum shifts to higher frequencies.

The effects of temperature on the spectra of the species susceptible to H_2 reduction are illustrated in Fig. 2. The spectra shown in this figure represent the difference between spectra taken under reaction conditions and those obtained following H_2 reduction of the catalyst at the reaction temperature. This mode of presentation is similar to that used in Fig. 1c, with the exception that bands associated with the gas phase and species weakly bound to the support are not subtracted out. The series of peaks occurring between 2300 cm^{-1} and 2060 cm^{-1} is due to gas phase CO . These bands are clearly evident in spectrum e, which was obtained at the conditions of spectrum b using a disk of alumina free of Ru. Both the position and intensity of the

Fig. 2 Spectra of chemisorbed CO under reaction conditions and following adsorption of CO: (a) sample spectrum - $H_2/CO = 2$, $P = 1$ atm, $T = 498K$; reference spectrum - after reduction in H_2 at 1 atm and 498K; (b) sample spectrum - $H_2/CO = 2$, $P = 1$ atm, $T = 523K$; reference spectrum - after reduction in H_2 at 1 atm and 523K; (c) sample spectrum - $H_2/CO = 2$, $P = 1$ atm, $T = 548K$; reference spectrum - after reduction in H_2 at 1 atm and 548K; (d) sample spectrum - after CO adsorption at 1 atm and 523K and elution of gas phase CO with He; reference spectrum - after reduction in H_2 at 1 atm and 523K; (e) sample spectrum - $H_2/CO = 2$, $P = 1$ atm, $T = 523K$; reference spectrum - after reduction in H_2 at 1 atm and 523K.

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Fig. 2.

band near 2000 cm^{-1} depend on the catalyst temperature. As the temperature increases, the band maximum shifts to lower frequencies and the intensity decreases.

In addition to the major features appearing at 2000 cm^{-1} , a broad band can be seen in Fig. 2, which extends between 1800 and 1200 cm^{-1} . Superimposed on this band are five more sharply defined bands at 1750 , 1590 , 1450 , 1390 , and 1370 cm^{-1} . Only the weak band at 1750 cm^{-1} is due to chemisorbed CO. Based upon the studies of Dalla Betta and Shelef (1) and King (4,5), the bands at 1590 , 1390 , and 1370 can be assigned to formate structures, and the band at 1450 cm^{-1} can be assigned to carbonate structures. Both types of species are formed on the alumina support and accumulate during reaction. Upon reduction of the catalyst in H_2 , the intensity of the bands associated with these spectra diminish. As a result, the background spectra used in obtaining the spectra presented in Fig. 2 show a decrease in the intensity of the formate and carbonate bands with increasing temperature, and, consequently these bands are emphasized in the difference spectra shown.

The similarity of spectra obtained under reaction conditions with those obtained by exposure of the catalyst to CO alone can be seen by comparison of spectra b and d in Fig. 2. The latter spectrum was obtained after passing CO over the catalyst for 5 min and then eluting the gaseous CO with He for 0.5 min. With the exception of the gas phase bands, which are not present in spectrum d, spectra b and d are virtually identical.

A more detailed illustration of features appearing on the low frequency side of the principle carbonyl band is shown in Fig. 3. This

spectrum is similar to spectrum d in Fig. 2 but was obtained at 448K. At this temperature the formate and carbonate structures are not removed upon reduction and consequently the bands associated with these species are subtracted out completely. The broad band between 1800 and 1200 cm^{-1} is now seen to be composed of two broad bands centered at approximately 1700 cm^{-1} and 1500 cm^{-1} . In addition, a definite shoulder can be observed at 1920 cm^{-1} , on the low frequency side of the band near 2000 cm^{-1} .

All of the bands observed in Figs. 1 and 2 are attenuated slowly upon passage of He over the catalyst and much more rapidly in the presence of H_2 . An illustration of these changes is shown in Fig. 4. Passage of He over the catalyst causes a slow decrease in the intensity of the principle band and a concurrent downscale shift in its position. More careful examination of spectra 1 through 4 reveals that initially intensity is lost from the high frequency portion of the principle adsorption band and from the peaks present below 1900 cm^{-1} . This observation is supported by spectrum 1 in Fig. 4c, which represents the difference between spectra 1 and 2 in Fig. 4a. With increasing time, the region from which intensity is lost shifts towards lower frequencies, indicating that the position of the high frequency component of the principle band shifts to lower frequencies as its intensity decreases. Eventually, though, intensity is lost from both the high and low frequency regions of the principle adsorption band and from the peak located near 1700 cm^{-1} . Spectra 2, 3, and 4 in Fig. 4c illustrates these changes.

XBL 812-7920

Fig. 3. Spectrum obtained following CO adsorption at 1 atm and 448K and elution of gaseous CO by He.

XBL 812-7934

Fig. 4. Effects of He and H₂ on the intensities of bands associated with adsorbed CO: adsorption conditions - P_{CO} = 3.3 atm, T = 498K; (a1) following exposure to a He flow at 498K for 0.5 min; (a2) 2.7 min; (a3) 14.0 min; (a4) 46.0 min; (a5) following exposure to a H₂ flow at 498K for 0.2 min; (a6) 0.5 min; (b4) same as (a4) expanded fourfold; (b5) same as (a5) expanded fourfold; (b6) same as (a6) expanded fourfold; (c1) difference between (a1) and (a2) expanded twofold; (c2) difference between (a2) and (a3) expanded twofold; (c3) difference between (a3) and (a4) expanded twofold.

The relationship between the position of the principle band and the relative integrated adsorbance of the band is shown in Fig. 5. If it is assumed that the extinction coefficient associated with this band is constant, then the abscissa in this figure is equivalent to a fractional surface coverage. The plot is seen to consist of two distinct branches. As the ratio A/A_s decreases from unity, ν_{CO} shifts from 2030 cm^{-1} to lower values but at an ever decreasing rate. When A/A_s reaches 0.55, the decrease in ν_{CO} accelerates. Finally, at $A/A_s = 0.2$, ν_{CO} reaches a value of 1950 cm^{-1} .

Figure 4 also shows that the reduction of preadsorbed CO in H_2 causes a very rapid decline in the intensity of the high frequency side of the principle band and of the broad band centered at 1700 cm^{-1} . As a consequence, the bands located at 1920 cm^{-1} and 1500 cm^{-1} can now be seen more clearly. Spectrum 3 in Fig. 4b shows that the bands are also attenuated as the duration of reduction is extended.

Assignment of Carbonyl Bands - The present results show that as many as six bands can be identified for chemisorbed CO, located at 2040, 2030-1950, 1920, 1750, 1700, and 1500 cm^{-1} . The assignment of these features to specific structures is examined next, following which the stability and reactivity of the various forms of adsorbed CO are discussed.

The strong band observed between 2030 and 1950 cm^{-1} falls within the range of frequencies (2085 to 1950 cm^{-1}) associated with linearly-bonded CO in Ru carbonyl complexes (9). As a result, it is reasonable to assign this band to linearly-adsorbed CO. This interpretation is further supported by recent EELS (10) and reflectance infrared (11)

XBL 812-7924

Fig. 5. Relationship between the frequency of the principle carbonyl adsorption band and the coverage by linearly adsorbed CO.

studies of CO adsorbed on a Ru (001) surface. The spectra obtained in these investigations exhibit a single band which shifts with increasing CO coverage from about 1980 cm^{-1} to as high as 2080 cm^{-1} , as a result of strong lateral interactions in the adlayer. LEED (10, 12-14) and ESDIAD (15) observations support the assignment of this band to linearly-adsorbed CO.

While the shift in band position with coverage, observed in the present work is of the same magnitude as that reported for CO adsorption on Ru (001) surfaces (10,11), the highest and lowest frequencies observed in the single crystal studies are notably higher than those shown in Fig. 5. This difference may be due to differences between the physical properties of alumina-supported Ru microcrystallites and bulk Ru metal. It is also possible that at least a part of the difference may be due to the presence of carbon on the surface of the supported Ru, formed by CO disproportionation. Carbon has been found to act as an electron donor and to enhance the back-donation of electronic charge from the metal to the π^* orbitals of CO (1). This would have the effect of weakening the C-O bond and shifting its frequency down-scale. It is significant to note, that while carbon deposition via CO disproportionation has been observed for alumina-supported Ru (16, 17), no evidence has been reported for the occurrence of this reaction on Ru (100), (001), (1010), (110) surfaces studied at low pressures (12,18-21).

As was noted earlier, during reaction the band near 2000 cm^{-1} undergoes a moderate (10-15%) growth in intensity which is unaccompanied by changes in the band position. A plausible explanation for this

observation is that the Ru dispersion increases slightly with time of reaction but that the fractional coverage of the surface remains the same. The fact that such changes are not observed upon exposure of the catalyst to CO alone and that the rate of change is accelerated by higher reaction pressure, at a fixed H_2/CO ratio and temperature, suggests that the changes in Ru dispersion may be caused by the local release of the heat of CO hydrogenation. Under this influence some of the smaller three-dimensional microcrystallites may be converted to two-dimensional rafts, thereby exposing a greater fraction of surface Ru atoms.

The spectra presented in Figs. 1 and 2 indicate that both the frequency and intensity of the band assigned to linearly-adsorbed CO decrease with decreasing CO partial pressure and catalyst temperature. Since, as was shown in Fig. 3, the spectra observed for CO chemisorbed in the presence and absence of H_2 are virtually identical, it seems reasonable to propose that the changes observed under reaction conditions can be ascribed to changes in the coverage of the Ru surface by linearly-adsorbed CO. Because of the increase in band intensity with duration of reaction, discussed above, band intensity cannot be used as a reliable measure of the coverage of linearly-bonded CO. An estimate of the fraction of the total sites which could be covered at saturation by this species can be attained, however, by assuming that the extinction coefficient for the band near 2000 cm^{-1} is independent of coverage and then using the relationship between frequency and coverage noted in Fig. 5. It should be noted, though, that the assumption underlying such calculations is not fully established. In studies

conducted by Pfnur et al. (11), the intensity of the infrared band associated with CO chemisorbed on a Ru (001) surface was found to increase linearly with CO coverages, up to a coverage of one half of saturation. For higher coverages, the integrated intensity declined. These results would suggest that the extinction coefficient decreases at coverages approaching saturation. However, since only a monotonic change in integrated intensity with coverage was observed in the present work, it can be concluded that the trend observed for a Ru (001) surface does not necessarily apply to alumina-supported Ru microcrystallites.

Applying the approach described above, a series of isotherms can be constructed to determine the coverage of linearly-adsorbed CO under reaction conditions. Figure 6 shows that on a plot of θ_{CO}^{-1} versus P_{CO}^{-1} the data fall along straight lines, independent of the H_2 partial pressure. Consequently θ_{CO} can be described by a Langmuir isotherm of the form

$$\theta_{\text{CO}} = \frac{K_{\text{CO}} P_{\text{CO}}}{1 + K_{\text{CO}} P_{\text{CO}}} \quad (1)$$

where K_{CO} is the effective equilibrium constant for CO adsorption.

From the slopes of the lines presented in Fig. 6 it is determined that

$$K_{\text{CO}} = 1.1 \times 10^{-9} \exp(25,500/RT) \text{atm}^{-1} \quad (2)$$

The heat of adsorption appearing in eqn. 2 is in excellent agreement with activation energies for CO desorption determined in studies conducted with alumina-supported Ru (17) and Ru single crystals (18-22).

XBL 812-7925

Fig. 6. Relationship between θ_{CO}^{-1} and P_{CO}^{-1} during reaction.

The preexponential factor, though, is two orders of magnitude smaller than that calculated from data presented by Pfnür et al. (22) for CO desorption from a Ru (001) surface at high CO coverages. A possible explanation for this difference may be that the frequency factor for CO desorption from the surface of alumina-supported Ru is two orders of magnitude higher than that for desorption from a Ru (001) surface.

The observations concerning the band for linearly-adsorbed CO reported here are in qualitative agreement with previous studies of a similar nature, but some differences exist with regard to the interpretation of the shifts in band position with reaction conditions. Working with a 5% Ru/Al₂O₃ catalyst, Dalla Betta and Shelef (1) reported that the spectrum of CO adsorbed at 523K from a 1 atm CO/He mixture (0.025:0.975 mole fraction) exhibited a single band centered at 2043 cm⁻¹. When the catalyst was contacted with an H₂/CO/He mixture (0.075:0.025:0.900) at the same temperature and pressure, the band shifted to 1996 cm⁻¹, and the integrated band intensity decreased by 12%. A similar effect of H₂ was noted by King (4) in studies performed with a 1% Ru/Al₂O₃ catalyst. Dosing the catalyst with CO at room temperature produced a band at 2045 cm⁻¹ which shifted to 2020 cm⁻¹ following exposure of the adsorbed CO to an H₂ pressure of 5.4 atm. Both Dalla Betta and Shelef (1) and King (4) have proposed that the shift in CO frequency could be attributed to an increase in the availability of electrons for back-bonding from the metal to the adsorbed CO, resulting from the presence of coadsorbed H atoms. While this interpretation is plausible, it seems that one could equally well explain these observations in terms of a decrease in the dipole-dipole interactions

resulting from a small change in the surface coverage by CO (11). As may be seen in Fig. 5, a 15% decrease in the integrated absorbance of the band from its maximum value corresponds to a shift in the band from 2030 cm^{-1} to 2000 cm^{-1} .

Dalla Betta and Shelef (1) and King (4) reported that increasing the temperature while passing a continuous flow of H_2 and CO over the catalyst caused a downscale shift in the position of the band for linearly-adsorbed CO and a reduction in the band intensity. Provided temperatures did not exceed $\sim 523\text{K}$ and reaction times were relatively short, the initial CO band could be restored simply by cooling the catalyst in the following H_2/CO mixture. At higher temperatures and with durations of reaction exceeding several hours, much of the CO band intensity remained lost upon cooling. Dalla Betta and Shelef (1) associated the irreversible changes in CO band position and intensity to the interaction of the metal with a carbonaceous deposit. King (4) concurs with this explanation but suggests that the reversible changes in the band characteristics are due to depletion via reaction of more weakly bound forms of CO which exhibit adsorptions towards the high frequency side of the CO band.

In the present study the duration of reaction was kept to less than 20 min and the temperature never exceeded 548K , in order to avoid extensive catalyst deactivation due to the build up of carbon. As a result, it is believed that the changes in CO band frequency and intensity with temperature shown in Fig. 2 are not due to the accumulation of carbon on the catalyst surface but, rather, to changes in the coverage of linearly-adsorbed CO.

The bands observed at 2040 and 1960 cm^{-1} in the present work are very similar to those reported by Kuznetsov et al. (7) in their studies of the structures formed upon decomposition of alumina-supported $\text{Ru}_3(\text{CO})_{12}$, $\alpha\text{-H}_4\text{Ru}_4(\text{CO})_{12}$, and $\text{Ru}_6\text{C}(\text{CO})_{17}$. In each case, reduction of the supported cluster in H_2 at temperatures less than 573K led to the appearance of two bands of nearly comparable intensity, located at 2047-2052 and 1965-1970 cm^{-1} . Comparison of the positions of these bands with those for Ru-halocarbonyl complexes leads to the conclusion that the two bands arise from structures of the form $[\text{Ru}(\text{CO})_2\text{X}_2]_n$ (7,9). The element X in this structure is assumed to be the oxygen of the alumina lattice and the number n represents the number of Ru atoms present in the surface structure.

Consistent with the proposed interpretation, the bands appearing at 2040 and 1960 cm^{-1} can be associated with the symmetric and asymmetric modes of vibration of C-O bonds in a pair of CO molecules attached to a common Ru site. The angle between the two CO molecules, 2α , can be estimated from the ratio of the integrated adsorbances of the symmetric and asymmetric bands, A_{sym} and A_{asym} , by means of eqn. 3 (23-25).

$$A_{\text{asym}}/A_{\text{sym}} = \tan^2 \alpha \quad (3)$$

This relationship has been shown to provide an accurate measure of α for dicarbonyl transition metal complexes in which the two CO ligands are in a cis configuration. Application of eqn. 3 to the bands at 1960 and 2040 cm^{-1} leads to an estimate of $100^\circ \pm 5^\circ$ for the angle between the two CO molecules attached to a common Ru site. By way of compari-

son, it is noted that bond angles between 93 and 96° have been reported for $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and a bond angle of 91° has been reported for $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ (24,26). Thus, it appears that the angle between diadsorbed CO molecules is similar to that found for transition metal complexes.

The independence of the vibrational frequencies associated with the diadsorbed CO structures on the coverage by singly-adsorbed CO indicates that the two structures are, most likely, not coupled by dipole-dipole interactions (25). This observation, together with the fact that the diadsorbed CO is much more stable to decomposition or reduction than monoadsorbed CO, suggest that the diadsorbed structures occur at sites isolated from the Ru crystallites. Examples of such sites might be individual Ru atoms or small Ru clusters. This interpretation is supported by the fact that the intensity of the bands at 2040 and 1960 cm^{-1} can be attenuated significantly by extended exposure of the catalyst to CO without affecting the intensities or positions of other CO bands (27).

The band appearing at 1920 cm^{-1} in Fig. 5b occurs at a frequency about 30 cm^{-1} lower than that normally ascribed to linearly-bonded CO in unsubstituted Ru carbonyls. However, C-O vibrational frequencies as low as 1900 cm^{-1} have been observed for linearly-bonded CO in Ru carbonyl complexes containing nucleophilic ligands (9). In view of this, the band at 1920 cm^{-1} can be assigned to CO adsorbed in a linear mode at a site adjacent to a nucleophilic adsorbate. The most likely candidate for the latter species is carbon, formed as an intermediate in either CO disproportionation or hydrogenation.

The weak peak at 1750 cm^{-1} and the broad peaks at 1700 and 1500 cm^{-1} appear at frequencies much lower than those normally associated with bridging carbonyls ($1880\text{--}1813\text{ cm}^{-1}$) in Ru complexes (9). Recent studies have shown that CO vibrations do occur in this portion of the spectrum for μ -bonded carbonyls, in which coordination occurs through both the carbon and oxygen atoms of CO, and for adducts formed between metal carbonyls and Lewis acids. When coordination takes place exclusively with metal atoms, CO frequencies of 1645 cm^{-1} for $\text{Mn}_2(\text{CO})_5(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2$ (28) and 1330 cm^{-1} for $(\eta^5\text{-C}_5\text{H}_5)_3\text{Nb}_3(\text{CO})_7$ (29) have been observed. The large difference in these frequencies reflects the fact that μ -bonding can occur in different ways. In the case of adducts of metal carbonyls with Lewis acids, C-O stretching frequencies are observed in the range of $1530\text{--}1700\text{ cm}^{-1}$ (9,30). In the case of $\text{Ru}_3(\text{CO})_{12}\cdot\text{AlBr}_3$, a strong band is seen at 1535 cm^{-1} and spectra of the 1:1 and 1:2 adducts of $[(\pi\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$ with isobutyl aluminum exhibit a band at 1680 cm^{-1} (9,30).

Reactivity of Carbonyl Structures - The spectra presented in Figs. 1 and 3 demonstrate that the different forms of adsorbed CO exhibit significant differences in reactivity with respect to H_2 . The two types of linearly-adsorbed CO, which are characterized by the band appearing between 2030 and 1950 cm^{-1} and the band appearing at 1920 cm^{-1} , react rapidly with H_2 . Transient response experiments (31) have shown that the dynamics of the disappearance of these bands correlate closely with the formation of methane and water, which suggests that linearly-adsorbed CO is the primary source of carbon for the synthesis reaction. Figure 3 shows that the band at 1700 cm^{-1} is also attenuated rapidly

during H_2 reduction. No study has been made of the reaction dynamics associated with this band and hence it is not possible to conclude whether the μ -bonded form of CO which this band represents is an important reaction precursor.

The pair of bands at 2040 and 1960 cm^{-1} are relatively stable to reduction and attenuate only slowly at temperatures below 548K. This fact, plus the general behavior of these bands, suggests that diadsorbed CO does not enter into the synthesis of hydrocarbons under the reaction conditions examined in these studies. Consistent with this conclusion, it has been found (27) that catalysts which exhibit a high proportion of diadsorbed CO relative to singly adsorbed CO are less active than catalysts which exhibit the reverse relationship between the two forms of adsorbed CO. The μ -bonded form of CO characterized by the band at 1500 cm^{-1} is only slightly less reactive than the linearly-adsorbed form of CO. However, because of the weak intensity of this band it has not been possible to relate the intensity of this band to the catalyst activity.

Bands Observed Between 3200 and 2400 cm^{-1}

Figure 7 shows a sequence of spectra for the frequency range between 3200 and 2400 cm^{-1} , taken at different times during the course of a run. The spectrum taken after 0.5 min shows only a very noisy baseline due to the poor transmission of the catalyst disk in this frequency regime. After 10 min of reaction, well defined peaks can be detected at 2930 and 2860 cm^{-1} . The intensity of these features increase steadily with time and after 20 min a shoulder can be detected at 2960 cm^{-1} in addition to the two more intense bands. It is signifi-

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Fig. 7. Effects of reaction duration on the intensities of bands appearing between 2400 and 3200 cm⁻¹: H₂/CO = 3; P = 1 atm; T = 498K.

cant to note that over the same period of time the intensity of the principle CO band increases by less than 8% and its position remains fixed at 2010 cm^{-1} .

Spectra of the C-H stretching region taken at different temperatures, pressures, and H_2/CO ratios exhibit the same set of bands observed in Fig. 7. By way of illustration, three spectra are shown in Fig. 8, taken after 10 min of reaction at temperatures of 498, 523, and 548K; a pressure of 10 atm; and an H_2/CO ratio of 2. It is seen that the positions of the three bands remain fixed and are insensitive to changes in the reaction conditions. The increase in band intensities with increasing temperature can be associated with the more rapid rate of accumulation of species adsorbing infrared radiation in this portion of the spectrum.

The stability of the bands seen in Figs. 7 and 8 were examined by treating the catalyst in various gas mixtures following reaction. Purging the reactor with He or a CO/He mixture at reaction temperature had no effect on the band intensities. The bands were rapidly attenuated, though, when a H_2/He mixture was introduced into the reactor. The rate of attenuation was found to increase with increasing catalyst temperature and H_2 partial pressure.

Efforts were also made to determine whether the features appearing in Figs. 7 and 8 might be associated with reactions occurring on the alumina support. Passage of H_2/CO mixtures over an alumina disk failed to produce any bands over the temperature interval of 498 to 548K. Weak bands were observed, though, when an alumina disk was placed in a cell immediately downstream of the cell containing the catalyst disk.

XBL 812-7910

Fig. 8. Effects of temperature on the intensities of bands appearing between 2400 and 3200 cm^{-1} : $\text{H}_2/\text{CO} = 2$; $P = 10$ atm; observation time = 10 min.

Since the positions of the bands were identical to those observed in Figs. 7 and 8, these bands most likely arise from the adsorption of hydrocarbon products on the alumina disk.

The positions of the three bands found here are virtually identical to those which have been reported by Dalla Betta and Shelef (1), Ekerdt and Bell (2,3), and King (4,5) in studies of CO hydrogenation over alumina- and silica-supported Ru catalysts. The bands at 2930 and 2861 cm^{-1} can be assigned to the asymmetric and symmetric stretching of CH_2 groups present in saturated compounds, and the shoulder at 2960 cm^{-1} can be assigned to a methyl group (9). It is significant to note that in contrast to the work carried out by King (4,5) with a $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst, the position of the bands did not shift upscale with increasing reaction temperature and no hydrocarbon structures were formed by the interaction of CO and H_2 over alumina devoid of Ru.

Based on infrared spectra taken during CO hydrogenation over a $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst, Dalla Betta and Shelef (1) concluded that the hydrocarbon bands observed could be ascribed to reaction products accumulated on the alumina support. The results of the present study also agree with this interpretation. The monotonic growth of the hydrocarbon bands beyond the point at which steady state reaction has been attained, and the absence of any influence of the hydrocarbon band growth on the position or intensity of the CO band indicates that the hydrocarbon species are unlikely to be on the Ru surface. Adsorption on the support is indicated by the observation of hydrocarbon bands on an alumina disk placed downstream of a catalyst disk and the report of similar bands when ethylene is adsorbed on η -alumina (32). Since α -olefins are the

dominant C_{2+} hydrocarbons formed under the reaction conditions chosen for this study (6), it is reasonable to expect that the structures observed in the infrared spectra arise from the adsorption of these products at acid sites on the catalyst support. The carbonium ion thus formed would be stable in the absence of significant atomic hydrogen on the support surface. Since the surface of Ru is virtually saturated with CO under reaction conditions little hydrogen-spillover to the support would be expected. However, upon elimination of CO from the gas stream, the metal surface rapidly clears of adsorbed CO, and hydrogen can now adsorb freely. Spillover of hydrogen from the Ru to the alumina would then provide a source of atoms for removal of the adsorbed hydrocarbons.

CONCLUSIONS

The results of in situ infrared spectroscopy presented here demonstrate that the surface of a Ru/Al_2O_3 catalyst is covered primarily by linearly-adsorbed CO. The coverage by this species depends on the catalyst temperature and the CO partial pressure, and is found to obey a Langmuir isotherm, characterized by an equilibrium constant of $K_{CO} = 1.1 \times 10^{-9} \exp(25,000/RT) \text{ atm}^{-1}$. Moderate concentrations of diadsorbed CO (e.g., $Ru(CO)_2$) and small concentrations of μ -bridge adsorbed CO (e.g., $Ru-CO-Ru$) were observed in addition to the linearly-adsorbed form. The first of these species appears to be associated with either individual Ru atoms or small Ru clusters, which interact strongly with the alumina support. In contrast to the linearly-adsorbed form of CO, diadsorbed CO does not react with H_2 at temperatures below 548K, and hence does not appear to participate in CO

hydrogenation. The μ -bridged form of CO may occur in one of two possible forms. The first would be between a pair of Ru atoms, such that one atom bonds to the carbon end and the other Ru atom bonds to the oxygen end of the molecule. The second possibility is that the CO is attached through its carbon end to a Ru site and that the oxygen end interacts with a Lewis acid site on the support. Unfortunately, the amount of μ -bridge adsorbed CO detected is too small to make any definitive conclusions regarding its role in CO hydrogenation.

Bands associated with adsorbed hydrocarbon, formate and carbonate structures were also observed. The behavior of the hydrocarbon bands during and after reaction suggest that these structures are formed by the adsorption of olefinic hydrocarbons on the support. On the other hand, it appears that the formate and carbonate structures are formed on the surface of the alumina support via reactions of CO and H_2 .

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CHAPTER IV

The Kinetics and Mechanism of Carbon Monoxide
Hydrogenation Over Alumina-Supported Ruthenium

ABSTRACT

A study was conducted of hydrocarbon synthesis from CO and H₂ over an alumina-supported Ru catalyst. Rate data for the formation of methane and C₂ through C₁₀ olefins and paraffins were fitted by power law rate expressions. The kinetics observed experimentally can be interpreted in terms of a comprehensive mechanism for CO hydrogenation, in which CH_x (x=0-3) species play a primary role. Expressions for the kinetics of methane synthesis, the kinetics and distribution of C₂₊ olefins and paraffins, and the probability of hydrocarbon chain growth derived from this mechanism are found to be in good agreement with the experimental results. The observed deviations from theory can be ascribed to secondary processes such as olefin hydrogenation and paraffin hydrogenolysis.

INTRODUCTION

During the past decade, extensive efforts have been made to understand the mechanism by which Group VIII metals catalyze the synthesis of hydrocarbons from CO and H₂ (1-7). One of the most important results of these investigations has been to draw attention to the importance of nonoxygenated surface intermediates. An increasing body of evidence now supports the hypothesis that hydrocarbon synthesis is initiated by the dissociation of CO and that the carbon atoms thus produced are hydrogenated to form adsorbed methylene and methyl groups. It has been proposed (5-7) that methyl groups act as precursors for the formation of methane as well as the growth of hydrocarbon chains, the latter process beginning with the insertion of a methylene group into the metal-carbon bond of a methyl group. Chain growth can continue by the further addition of methylene units to adsorbed alkyl species. Olefins and paraffins are finally produced from the alkyl moieties by either hydrogen elimination or addition.

A substantial part of the evidence supporting this view of hydrocarbon synthesis has been obtained from studies conducted with ruthenium catalysts. The emphasis on this metal can be explained by the fact that ruthenium produces, primarily, linear olefins and paraffins and relatively few oxygenated products. Moreover, unlike iron and cobalt, ruthenium is not converted to a carbide under reaction conditions. Studies by several authors (8-11) have shown that chemisorbed CO will dissociate on ruthenium at elevated temperatures to form adsorbed carbon atoms. Hydrogenation of this carbon occurs very readily to form methane as well as higher molecular weight paraffins. Ekerdt and Bell

(12) have shown that carbon deposition also takes place during the steady-state reaction of CO and H₂, and that hydrogenation of this carbonaceous deposit following the elimination of chemisorbed CO produces a spectrum of hydrocarbon products. These latter results demonstrate that chain growth can occur in the absence of adsorbed CO. Further evidence for the participation of atomic carbon in the growth of hydrocarbon chains has been obtained by Biloen et al. (11). In these studies nickel, cobalt, and ruthenium catalysts were precovered with ¹³C atoms produced by the disproportionation of ¹³CO. The adsorbed ¹³CO was exchanged with ¹²CO and the catalysts were then exposed to a mixture of ¹²CO and H₂. Careful mass spectrometric analysis of the products showed a random distribution of ¹²C and ¹³C among the hydrocarbons, consistent with the initial inventories of the two isotopes. It was also found that the time needed to convert ¹³C atoms and ¹²CO molecules to methane were nearly identical. From these observations it was concluded that CO dissociation is very rapid and hence is unlikely to be a rate limiting step, that CH_x (x = 0-3) species constitute the most reactive C₁ surface species, and that methane and other hydrocarbons are formed from the same building blocks. These conclusions have also been supported by the analysis of methane synthesis kinetics reported by Ekerdt and Bell (12) and by the observation of a significant inverse H₂/D₂ isotope effect on methane synthesis recently reported by Kellner and Bell (13).

The proposition that hydrocarbon chain growth can occur on a ruthenium surface via a polymerization mechanism involving methylene groups as the monomer has recently been supported by the work of Brady

and Petit (14). These authors demonstrated that a spectrum of hydrocarbons, resembling that obtained by CO hydrogenation, can be formed by reaction of CH_2N_2 and H_2 over ruthenium and other Groups VIII metals. The results were explained by suggesting that the decomposition of CH_2N_2 acts as a source of methylene groups, a part of which is converted to methyl groups by reaction with adsorbed hydrogen. It was proposed that the methyl groups then act as initiators for chain growth. The applicability of these results and their interpretation to hydrocarbon synthesis from CO and H_2 is supported by the work of Bell and coworkers (15,16). Their work has shown that methyl, methylene, and higher molecular weight alkyls present on a ruthenium surface can be detected through the reaction of these species with olefins, and that the consumption of surface methylene groups by this means inhibits the propagation of hydrocarbon chain growth.

In the present study an investigation has been carried out of the kinetics of hydrocarbon synthesis over an alumina-supported ruthenium catalyst. Emphasis was placed on establishing the influence of reaction conditions on the rates of product formation, the distribution of olefins and paraffins according to carbon number, and the ratio of olefin to paraffin obtained for each carbon number. These data were then used to evaluate theoretical expressions for the reaction kinetics, derived from a comprehensive mechanism for hydrocarbon synthesis.

EXPERIMENTAL

A 1% Ru/Al₂O₃ catalyst was prepared by adsorption of Ru₆C(CO)₁₇ from pentane solution on to Kaiser KA-201 γ -alumina. Details concerning synthesis of the complex and the impregnation procedure have been described previously (17). Once dried, the catalyst was reduced in flowing H₂. Reduction was begun by slowly raising the temperature from 298 to 673K and continued by maintaining it at 673K for 8 hr. The dispersion of the reduced catalyst was determined to be 1.0 by H₂ chemisorption.

A stainless steel microreactor heated in a fluidized bed was used for all of the work reported here. Reactants were supplied from a high-pressure cylinder containing a desired ratio of H₂ and CO. The reaction products were analyzed by gas chromatography using flame ionization detection. A balanced pair of 2.4 mm by 1 m stainless steel columns packed with Chromsorb 106 was used to separate C₁ through C₅ paraffins and olefins. A 0.25 mm by 35 m glass capillary column coated with OV-101 was used to separate C₅ through C₁₀ paraffins and olefins. Complete product distributions were determined by normalizing the analyses for the C₅ products obtained from the packed and capillary columns.

Prior to each series of experiments, the catalyst (100 mg) was reduced in flowing H₂ for 10 to 12 hr at 673K and 10 atm. The temperature was then lowered to 498K and the feed mixture was introduced at a flow rate of 200 cm³/min (NTP). Ten minutes after the reaction had begun, a gas sample was taken for analysis and the gas feed was switched over to pure H₂ for 1 hr. By alternating short reaction periods and

longer reduction periods, a stable catalyst activity could be achieved after several cycles. Once this condition had been obtained the reaction conditions were adjusted to those desired for a particular experiment. Periodically, data were taken at 498K, 10 atm, and $H_2/CO = 3$ to determine whether changes in catalyst activity had occurred. In all cases, activities were reproduced to within a few percent. Maintaining the catalyst in H_2 for prolonged periods was also determined to have no effect on catalyst activity.

RESULTS

The rate of methane formation was measured at pressures between 1 and 10 atm, temperatures between 448 and 548K, and H_2/CO ratios of 1, 2, and 3. The accumulated data were fitted, by means of a nonlinear least squares regression, to the power law expression given by eqn. 1,

$$N_{C_1} = 1.3 \times 10^9 \exp(-28,000/RT) P_{H_2}^{1.35} / P_{CO}^{0.99} \quad (1)$$

In this equation, N_{C_1} is the rate of methane formation per second per surface Ru site, and P_{H_2} and P_{CO} are the partial pressures of H_2 and CO, respectively, expressed in atmospheres. Figure 1 illustrates the quality of agreement between rates calculated using eqn. 1 and those determined experimentally. The average deviation between experiment and correlation is less than $\pm 6\%$.

Seventy to eighty percent of the hydrocarbon products were analyzed to be C_2 through C_{10} paraffins and olefins. Examples of the ratio of the formation of hydrocarbons containing n carbon atoms to the rate of methane formation are shown in Figs. 2 and 3. Figure 2 shows that

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Fig. 1. Cross-plot of predicted versus observed rates of methane synthesis.

Fig. 2. Distribution of C_1 through C_{10} hydrocarbons observed at 1 atm: a) effects of H_2/CO ratio; b) effects of temperature.

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Fig. 3. Distribution of C_1 through C_{10} hydrocarbons observed at 10 atm: a) effects of H_2/CO ratio; b) effects of temperature.

with the exception of the points for $n=2$ all of the data taken at 1 atm lie along straight lines on the coordinates of $\log (N_{C_n}/N_{C_1})$ versus $(n-1)$. The increasing slope of the lines as either the H_2/CO ratio or the temperature is decreased is indicative of an increase in the average molecular weight of the products. The data taken at 10 atm (Fig. 3) also lie along straight lines on the indicated coordinates, but in this case deviations are seen for $n = 2$ and 3. When either the H_2/CO ratio or the temperature is decreased, the slope of the lines in Fig. 3 increase slightly, and the lines appear to be translated upwards in a near parallel fashion.

The kinetics for the synthesis of C_2 through C_{10} olefins and paraffins can also be represented by power law rate expressions. Parameter values obtained by fitting the data to such expressions are presented in Tables I and II. Examination of Table I shows that a positive order dependence on H_2 and a negative order dependence on CO partial pressures is observed in all cases. For a given carbon number, the H_2 dependence for paraffin formation is higher than that for olefin formation, whereas the CO dependence is more nearly the same for both products. The data in Table II also indicate that the magnitudes of m and n for the formation of olefins decrease substantially with increasing carbon number. While there is some indication of a similar trend for the paraffins, the pattern is not as clearly evident as for the olefins.

The information presented in Table II shows that the activation energy for olefin synthesis is higher than that for paraffin synthesis, suggesting that the olefin to paraffin ratio in the products

Table I. Dependencies of the Rates for the Synthesis of C_1 through C_{10} hydrocarbons on the Partial Pressures of H_2 and CO^a .

C_n	m	Olefin n	% Dev. ^b	m	Paraffin n	%Dev. ^b
C_1	-	-	-	1.31	-0.96	7.7
C_2	0.82	-0.73	4.8	1.45	-0.85	7.7
C_3	0.80	-0.55	3.2	1.37	-0.49	4.9
C_4	0.74	-0.47	3.0	1.21	-0.46	3.3
C_5	0.53	-0.36	8.1	0.86	-0.24	2.3
C_6	0.47	-0.28	6.3	1.11	-0.32	13.5
C_7	0.35	-0.19	9.3	0.94	-0.24	5.9
C_8	0.31	-0.15	11.5	0.91	-0.27	7.9
C_9	0.20	-0.05	12.3	0.50	-0.18	19.4
C_{10}	0.17	-0.01	15.4	0.93	-0.35	11.4

^aReaction conditions: $T = 498K$; $P = 1-10$ atm; $H_2/CO = 1-3$

^bAverage deviation between predicted and observed rates.

Table II. Power Law Rate Expressions^a for the Synthesis of C₁ through C₄ Hydrocarbons^b.

C _n	[A atm ^(m-n) s ⁻¹]	m	n	E _a (kcal/mole)	%Dev. ^c
C ₁	1.3 x 10 ⁹	1.35	-0.99	28	5.6
=					
C ₂	2.5 x 10 ⁸	0.74	-0.68	28	5.7
=					
C ₂	1.6 x 10 ⁶	1.34	-0.81	25	11.3
=					
C ₃	2.3 x 10 ⁷	0.82	-0.58	25	4.2
=					
C ₃	1.4 x 10 ³	1.39	-0.55	18	5.8
=					
C ₄	3.8 x 10 ⁶	0.70	-0.44	24	9.6
=					
C ₄	8.7 x 10 ³	1.14	-0.47	19	4.8

^a

$$N_{C_n} = A \exp(-E_a/RT) P_{H_2}^m P_{CO}^n$$

^b
Reaction conditions: T = 448-548K; P = 1-10 atm; H₂/CO = 1-3.

^c
Average deviation between predicted and observed rates

should increase with increasing temperature. The extent to which this trend is observed is illustrated in Fig. 4. Below about 498K, the plots of $\log (N_{C_n=}/N_{C_n-})$ versus $1/T$ are linear for $n = 2, 3$, and 4. From the slope of this portion of the plots, the difference in activation energies for the formation of olefins and paraffins is estimated to be about 6 kcal/mole. The sharp decline in $\log (N_{C_n=}/N_{C_n-})$ which occurs at temperatures above 498K can be ascribed to hydrogenation of the olefins. This interpretation was confirmed by examining the effects of reactant space velocity on the olefin to paraffin ratio. At temperatures below 498K, this ratio is independent of space velocity, but as the temperature is increased above 498K, the ratio of olefins to paraffins decreases with decreasing space velocity.

Since it has been reported that olefins formed via primary reactions can be reincorporated to form higher molecular weight products (7,15), an investigation was made to establish the possible influence of such reactions on the observed product distributions. When ethylene was added to the synthesis gas at levels similar to those produced by the reaction, no evidence could be observed for olefin reincorporation. Raising the level of ethylene addition to 0.5 or 1.0% of the total feed (20 to 40 times that normally found in the reaction products) did produce an effect on the distribution of products, as can be seen in Fig. 5. The formation of C_3 and C_4 products is increased, but the formation of C_{6+} products is suppressed. The extent to which these changes occur increases with the level of ethylene addition. A similar trend was also observed for data taken at 1 atm and 498K.

Fig. 4. Effects of temperature on the olefin to paraffin ratio of C_2 through C_4 products: a) $P = 1$ atm; b) $P = 10$ atm.

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Fig. 5. Effects of ethylene addition on the distribution of C₁ through C₁₀ hydrocarbons.

DISCUSSION

The kinetics of hydrocarbon synthesis presented here can be interpreted in terms of the mechanism shown in Fig. 6. Detailed discussions of the experimental evidence supporting this view of CO hydrogenation have recently been presented in a number of reviews (1-7). Consequently, the justification for including particular steps, and for assuming that certain of these are reversible, will be restricted to ruthenium.

It is proposed that CO is first adsorbed into a molecular state from which dissociative adsorption can then occur. Infrared studies reported by a number of authors (12,18-20) indicate that the surface of Ru is nearly saturated by molecularly adsorbed CO under reaction conditions. The reversibility of molecular adsorption is supported by recent isotopic substitution studies performed with ^{12}CO and ^{13}CO which indicate that equilibration of the surface with the gas phase is very rapid under reaction conditions (21). Low and Bell (10) have shown that CO disproportionation will occur to a significant degree over $\text{Ru}/\text{Al}_2\text{O}_3$ for temperatures in excess of 423K. These results suggest that CO dissociation is an activated process. More recently, TPD experiments performed by McCarty and Wise (22) have demonstrated that the recombination of carbon and oxygen atoms and the desorption of CO are very rapid since extensive scrambling of preadsorbed $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ was observed at temperatures above 473K, where hydrocarbon synthesis normally occurs.

The adsorption of H_2 is assumed to occur dissociatively, and to be reversible. This view is supported by H_2/D_2 scrambling studies

Fig. 6. Proposed mechanism of hydrocarbon synthesis from CO and H₂.

performed in the presence of CO over a Ru/SiO₂ catalyst (21). The results of these experiments show that above 423K, the extent of scrambling is very close to that predicted at equilibrium, indicating that the rates of H₂(D₂) adsorption, reaction, and desorption are faster than the rate of hydrocarbon synthesis.

It is well recognized that during CO hydrogenation over Ru, water is the primary product via which oxygen is removed from the catalyst surface (12). The mechanism of forming water in the presence of substantial amounts of adsorbed CO is not known and may occur via either a sequence of Langmuir-Hinshelwood steps or a concerted Rideal-Eley step. For the purposes of the present discussion it has been assumed that the latter process represents the dominant reaction path.

The stepwise hydrogenation of single carbon atoms is taken as the starting point for hydrocarbon synthesis. Studies by a number of investigators (9-11) have shown that atomic carbon produced by either CO disproportionation or CO hydrogenation is extremely reactive and will form methane and higher molecular weight hydrocarbons upon hydrogenation. Furthermore, the work of Biloen et al. (11) has demonstrated that the incorporation of carbon into hydrocarbons occurs with equivalent ease from molecularly adsorbed CO and atomically adsorbed C, indicating that the dissociation of adsorbed CO is not a rate limiting step in the formation of hydrocarbons.—This conclusion is supported further by the recent studies of Kellner and Bell (13) in which evidence was reported for a strong inverse H₂/D₂ isotope effect on the synthesis of methane over two Ru/Al₂O₃ catalysts and a similar albeit weaker effect for synthesis over a Ru/SiO₂ catalyst. The authors noted that

the more rapid formation of CD_4 than CH_4 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 metal-carbon 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 β -elimination of hydrogen to form α -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

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 preceding 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 of 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

$$\theta_v = \frac{1}{K_1 P_{CO}}, \quad (1)$$

where K_1 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_{C_1} , can be written as

$$N_{C_1} = k_8 \theta_{CH_3} \theta_H, \quad (2)$$

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

$$\theta_{CH_3} = K_2^{1.5} K_3^{1.5} K_5 K_6 K_7 \frac{P_{H_2}^{1.5}}{P_{CO}} \frac{\theta_v}{\theta_0} \quad (3)$$

where K_i is the equilibrium constant for the i -th reaction and θ_0 is the fractional coverage of the Ru surface by O atoms. The magnitude of θ_H is given by

$$\theta_H = K_3^{1/2} \frac{P_{H_2}^{1/2}}{P_{CO}} \theta_v \quad (4)$$

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

$$N_{C_1} = k_8 \frac{K_2^{1.5} K_3^{1.5} K_5 K_6 K_7}{K_1^2 \theta_0} \frac{P_{H_2}^2}{P_{CO}^2} \quad (5)$$

The dependence of N_{C_1} on θ_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

$$N_{H_2O} = \sum_{n=1}^{\infty} n N_{C_n} \quad (6)$$

where

$$N_{H_2O} = k_4 \theta_0 P_{H_2} \quad (7)$$

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

$$\sum_{n=1}^{\infty} n N_{C_n} = k_8 \theta_{CH_3} \theta_H + \sum_{n=1}^{\infty} k_p \theta_{CH_2} \theta_n \quad (8)$$

where k_p is the rate constant for chain growth, step 9; θ_{CH_2} is the fractional coverage of the Ru surface by methylene groups; and θ_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.

$$k_4 \theta_0 P_{H_2} = k_8 \theta_{CH_3} \theta_H + \sum_{n=1}^{\infty} k_p \theta_{CH_2} \theta_n \quad (9)$$

Equation 9 can be solved for θ_0 in the limits where either methane or higher molecular weight products predominate. For the first case

$N_{C1} \gg \sum_{n=2}^{\infty} n N_{Cn}$. Substitution of the expressions for θ_{CH_3} and θ_H into eqn. 9 results in

$$\theta_0 = \frac{K_3}{K_1} \left(\frac{k_8}{k_4} K_2 K_5 K_6 K_7 \right)^{1/2} \frac{P_{H_2}^{1/2}}{P_{CO}} \quad (10)$$

which, on substitution into eqn. 5, gives

$$N_{C1} = k_e \frac{P_{H_2}^{1.5}}{P_{CO}} \quad (11)$$

where

$$k_e = \frac{K_3}{K_1} (k_8 k_4 K_2 K_5 K_6 K_7)^{1/2} \quad (12)$$

This result is identical to that obtained by Ekerdt and Bell (12).

For the second case, it is assumed that

$$N_{C1} \ll \sum_{n=2}^{\infty} n N_{Cn}$$

so that the first term on the right-hand side of eqn. 9 can be neglected. To solve for θ_0 in this case requires the development of expressions for θ_{CH_2} and θ_n . An expression for θ_{CH_2} can be derived from the equilibrium relationships existing between steps 1, 2, 3, 5 and 6. Thus

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

An expression for θ_n can be obtained by imposing a steady-state balance on the formation of alkyl groups containing n carbon atoms.

$$0 = k_p \theta_{n-1} \theta_{CH_2} - k_p \theta_n \theta_{CH_2} - k_{tp} \theta_n \theta_H - k_{to} \theta_n \theta_v \quad (14)$$

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 θ_n results in

$$\theta_n = \frac{k_p \theta_{CH_2} \theta_{n-1}}{k_p \theta_{CH_2} + k_{tp} \theta_H + k_{to} \theta_v} \quad (15)$$

Equation 15 can be rewritten in terms of the probability of chain propagation, α , as

$$\theta_n = \alpha^{n-1} \theta_{CH_3} \quad (16)$$

Comparing eqns. 15 and 16 shows that

$$\alpha = \frac{k_p \theta_{CH_2}}{k_p \theta_{CH_2} + k_{to} \theta_v + k_{tp} \theta_H} \quad (17)$$

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

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

If α 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 θ_0 can be obtained by substitution of eqns. 13 and 18 into eqn. 9. Thus,

$$\theta_0 = \left[\frac{k_p K_2^2 K_3^{2.5} K_5^2 K_6^2 K_7}{k_4 K_1^2 (1-\alpha)} \right]^{0.33} \frac{P_{H_2}^{0.5}}{P_{CO}^{0.67}} \quad (19)$$

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

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

where

$$k_e = k_8 \left[\frac{k_4 K_2^2 K_3^{2.5} K_5^2 K_6^2 K_7^2 (1-\alpha)}{k_p K_1^4} \right]^{0.33} \quad (21)$$

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 factors 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.

	Theory		Experiment			
	Eqn. 11	Eqn. 20	This Study	Dalla Betta et al. (23)	Vannice (24)	Ekerdt and Bell (12)
Catalyst	—	—	1% Ru/Al ₂ O ₃	1.5% Ru/Al ₂ O ₃	5% Ru/Al ₂ O ₃	5% Ru/SiO ₂
A atm ^(m-n) s ⁻¹	—	—	1.3 x 10 ⁹	3.2 x 10 ⁷	5.6 x 10 ⁸	2.2 x 10 ⁹
E _a (kcal/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

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 α -olefins can be expressed as follows:

$$N_{C_n}^- = k_{tp} \theta_H^n \theta_n \quad (22)$$

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

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 θ_n results in

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

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

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

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

$$\beta = \frac{k_{to}}{k_{tp} K_3^{1/2}} \quad (26)$$

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

$$\frac{N_{C_n}}{N_{C_1}} = \beta/P_{H_2}^{0.5} \quad (27)$$

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 car-

bon converted to hydrocarbons which contain n carbon atoms, f_n , should be given by

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

and, consequently, a plot of $\log(f_n/n)$ versus n should be a straight line of slope α 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.

$$f_n^- = \frac{nN_{C_n}^-}{\sum_{n=1}^{\infty} nN_{C_n}^-} \quad (29)$$

$$f_n^= = \frac{nN_{C_n}^=}{\sum_{n=2}^{\infty} nN_{C_n}^=} \quad (30)$$

Notice that the summation 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

$$f_n^- = n\alpha^{(n-1)}(1-\alpha)^2 \quad (31)$$

$$f_n^{\overline{}} = \frac{n\alpha^{(n-1)}(1-\alpha)^2}{1 - (1-\alpha)^2} \quad (32)$$

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 $f_n^{\overline{}}/n$ 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 $f_n^{\overline{}}/n$ 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 α 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 $f_n^{\overline{}}/n$ 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 $f_2^{\overline{}}/2$ 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 $f_2^{\overline{}}$ would correspond to the carbon number fraction of the

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

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

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

	P = 1 atm ^a		P = 10 atm ^a	
	Source	Value	Source	Value
α	Fig. 7	0.62	Fig. 8	0.61
α_b	Fig. 2	0.66	Fig. 3	0.63
f_1^-	Fig. 7	0.20	Fig. 8	0.23
f_1^-	$(1-\alpha)^2$	0.18	$(1-\alpha)^2$	0.17
f_1^-	$1-(1-\alpha)^2$		$[1-(1-\alpha)^2]$	
f_1^-	See note c	0.21	See note c	0.21
f_1^-	Fig. 7	0.66	Fig. 8	0.44
f_1^-	$(1-\alpha)^2$	0.14	$(1-\alpha)^2$	0.18
f_1^-	See note d	0.64	See note d	0.41

^aT = 498K; H₂/CO = 3

$$c \quad f_1^- = \frac{(1-\alpha)^2 / [1-(1-\alpha)^2]}{1-2 \left\{ (1-\alpha)^2 / [1-(1-\alpha)^2 - f_2^-/2] \right\}}$$

^bIntercept at (n-1) = 0

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

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_{2+} paraffinic product undergoes hydrogenolysis to form methane. Based on this interpretation, the correct value of f_1^- should be given by

$$f_1^- = (1-\alpha)^2 + \sum_{n=2}^{\infty} n \left[\alpha^{(n-1)} (1-\alpha)^2 - f_n^-/n \right] \quad (33)$$

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_2/CO ratio, elevation of the total pressure causes a reduction in θ_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 $N_{C_n}^-/N_{C_n}^-$ versus $P_{H_2}^{-0.5}$ should result in straight lines with a slope of β 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 β 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 β for $n = 2$ and 3 may be due, in part, to a partial hydrogenolysis of ethane and propane. The balance of the variation in β with n may be due to a dependence of the rate coefficients for chain termination on

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

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Fig. 10. Plot of β 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 β , 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, ΔH_{H_2} , by the following expression

$$E_{op} = E_o - E_p - \Delta H_{H_2}/2 \quad (34)$$

Assuming that ΔH_{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 α , the probability of chain growth, on the partial pressures of H_2 and CO can be determined starting from the definition for α , eqn. 17. Substitution of eqns. 1, 4, 13, and 19 for θ_v , θ_H , θ_{CH_2} , and θ_0 (assuming that $N_{C_1} \ll \sum_{n=2}^{\infty} nN_{C_n}$) gives the following expression:

$$\alpha = \left[1 + v(1-\alpha)^{-0.33} P_{CO}^{-0.67} (1 + \beta P_{H_2}^{-0.5}) \right]^{-1} \quad (35)$$

where

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

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

$$\alpha^{-1}(1-\alpha)^{1.33} = v_{\text{CO}}^{-0.67} (1 + \beta P_{\text{H}_2}^{-0.5}) \quad (37)$$

The utility of eqn. 37 as a representation for the dependence of α on the partial pressures of H_2 and CO , and on the temperature can now be examined. To do so requires that values of β and v be determined first. An expression for β can be obtained from the data presented in Figs. 4 and 10. Choosing the value of β for $n = 4$ as being representative leads to the following equation:

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

An equation for v can be obtained by forcing an agreement between eqn. 37 and the values of v determined at 1 atm for $\text{H}_2/\text{CO} = 2$ and temperatures of 498, 523, and 548K. The resulting expression is given by

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

A comparison between the experimental and predicted values of α is presented in Table V. It is observed that at 1 atm, eqn. 37 provides an accurate representation of the dependence of α on temperature as well as H_2 and CO partial pressures. When the total pressure is increased to 10 atm, eqn. 37 predicts values of α which are substantially higher than those observed experimentally. Nevertheless, the

Table V. Comparison of Predicted and Experimentally Observed Values of α .

P(atm)	T(K)	H_2/CO	α	
			Predicted	Experimental
1	548	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
		2	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

reduced dependence of α on H_2 and CO partial pressures observed at 10 atm is properly reflected.

The failure of eqn. 37 to provide an accurate estimation of α 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 α . A reaction which might contribute to such an effect would be the insertion of CO 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 α .

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_2 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 C_{2+} 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 of 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 α 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 proposed 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 silica-supported 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 Ru/SiO_2 and $\text{Ru/Al}_2\text{O}_3$ 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 H_2/CO and D_2/CO feed mixtures.

EXPERIMENTAL

Preparation of the 1.2% Ru/SiO_2 and 1.0% $\text{Ru/Al}_2\text{O}_3$ catalysts used in this study have been described in detail elsewhere (2,3). The initial dispersion of the alumina-supported catalyst determined by H_2 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_2 chemisorption since the uptake of H_2 , 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 validity of this assumption is supported by previous studies with low dispersion $\text{Ru/Al}_2\text{O}_3$ catalysts (5) and by

the observation that infrared spectra of CO adsorbed on the Ru/SiO₂ 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 H₂(D₂) and CO at a ratio of H₂(D₂)/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 CH₄ and CD₄.

Each experiment with a fresh catalyst charge (100 mg) was initiated by a 10 to 12 hr reduction in flowing H₂ at 673K and 10 atm. The temperature was then lowered to 498K and the feed mixture was introduced at a flow rate of 200 cm³/min (NTP). Ten minutes after the reaction began, a gas sample was taken for analysis and the gas feed was switched over to pure H₂ 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/SiO₂

The primary oxygen-containing organic product produced over the Ru/SiO₂ 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 H₂/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

$$N_{\text{CH}_3\text{CHO}} = 7.1 \times 10^2 P_{\text{H}_2}^{0.6} \exp(-15,000/RT) \quad (1)$$

and that for methane by

$$N_{\text{CH}_4} = 8.0 \times 10^9 P_{\text{H}_2}^{1.3} P_{\text{CO}}^{-1.0} \exp(-29,000/RT). \quad (2)$$

In both equations, the rates of acetaldehyde and methane synthesis, $N_{\text{CH}_3\text{CHO}}$ and N_{CH_4} , are expressed in molecules of product produced per second per Ru surface site, and the partial pressures of H₂ and CO, P_{H_2} and P_{CO} , are expressed in atmospheres. Deviations of less than ± 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 $\text{Ru/Al}_2\text{O}_3$ 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_4 formation is approximately 1.1 times that observed for CH_4 ; however, no isotope effect can be observed at 1 atm.

$\text{Ru/Al}_2\text{O}_3$

In contrast to the Ru/SiO_2 catalyst, the $\text{Ru/Al}_2\text{O}_3$ 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 approaches 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 formed decomposes back to CO and H_2 or reacts with the alumina support to form 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 H₂(D₂) and CO over a silica-supported Ru catalyst.

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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.

Fig. 3. Effect of reaction time on the rates of methane and methanol synthesis over an alumina-supported Ru catalyst.

Table I. The Effects of H_2/CO Ratio and Pressure on the Rates of Methanol and Methane Formation Over a 1.0% Ru/ Al_2O_3 Catalyst at 498K.

H_2/CO	P (Atm)	$N_{CH_3OH} (s^{-1})$	$N_{CH_4} (s^{-1})$
3	10	1.5×10^{-3}	2.5×10^{-3}
3	5	9.7×10^{-4}	2.0×10^{-3}
3	1	2.4×10^{-4}	1.3×10^{-3}
2	10	9.7×10^{-4}	1.4×10^{-3}
2	5	7.0×10^{-4}	1.1×10^{-3}
2	1	1.4×10^{-4}	6.6×10^{-4}
1	10	6.0×10^{-4}	8.7×10^{-4}
1	5	3.4×10^{-4}	6.7×10^{-4}
1	1	7.3×10^{-5}	4.0×10^{-4}

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Fig. 4. Arrhenius plots for the synthesis of methanol and methane from H₂(D₂) and CO over an alumina-supported Ru catalyst.

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 C₂₊ 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 β -hydrogen elimination from, or α -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)

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

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 $\text{CH}_3\text{RuCp}(\text{CO})_2$ 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 $\text{Os}(\text{CO})_2(\text{PPh})_3$ 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.

$$N_{\text{CH}_4} = k_8 \theta_{\text{CH}_3} \theta_{\text{H}} \quad (3)$$

$$N_{\text{CH}_3\text{CHO}} = k_{12} \theta_{\text{CH}_3} \theta_{\text{CO}} \quad (4)$$

where k_8 and k_{12} are the rate coefficients for reactions 8 and 12, respectively, and θ_{CH_3} , θ_{H} , and θ_{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 θ_{CH_3} , θ_{CO} , and θ_{H} can be represented by

$$\theta_{\text{CH}_3} = \left(\frac{k_4}{k_8} \right)^{1/2} (K_2 K_3 K_5 K_6 K_7)^{1/2} \frac{P_{\text{H}_2}}{\theta_{\text{CO}}} \quad (5)$$

$$\theta_{\text{CO}} = K_1 P_{\text{CO}} \theta_v \quad (6)$$

$$\theta_{\text{H}} = K_3^{1/2} P_{\text{H}_2}^{1/2} \theta_v, \quad (7)$$

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

$$\theta_{\text{CO}} \approx 1.0 \quad (8)$$

and

$$\theta_v = \frac{1}{K_1 P_{\text{CO}}} \quad (9)$$

Substitution of eqns. 5, 6, and 7 into eqns. 3 and 4, and elimination of θ_{CO} and θ_v from the resulting equations by substitution from eqns.

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

$$N_{\text{CH}_4} = \frac{K_3}{K_1} (k_8 k_4 K_2 K_5 K_6 K_7)^{1/2} \frac{P_{\text{H}_2}^{1.5}}{P_{\text{CO}}} \quad (10)$$

$$N_{\text{CH}_3\text{CHO}} = k_{12} \left(\frac{k_4}{k_8} \right)^{1/2} (K_2 K_3 K_5 K_6 K_7)^{1/2} P_{\text{H}_2} \quad (11)$$

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).

Comparison 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/SiO₂ 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^H/K_3^D based upon statistical mechanics (2) shows that $1.27 < K_3^H/K_3^D < 1.51$ for temperatures between 453 and 543K. Consequently, we can deduce from eqns. 7 and 9 that $\theta_H > \theta_D$.

Examination of eqn. 5 indicates that several factors will influence the relative magnitudes of θ_{CH_3} and θ_{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 θ_{CD_3} will be larger than θ_{CH_3} .

The isotope effects predicted for k_8 and θ_{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 obtain eqn. 12.

$$N_{CH_4} = \frac{k_8 K_3^{1/2}}{k_{12} K_1} \frac{P_{H_2}^{1/2}}{P_{CO}} N_{CH_3CHO} \quad (12)$$

The ratio $N_{\text{CH}_4}/N_{\text{CD}_4}$ can then be expressed as

$$\frac{N_{\text{CH}_4}}{N_{\text{CD}_4}} = \frac{k_8^{\text{H}}}{k_8^{\text{D}}} \left(\frac{K_3^{\text{H}}}{K_3^{\text{D}}} \right)^{1/2} \frac{N_{\text{CH}_3\text{CHO}}}{N_{\text{CD}_3\text{CDO}}} \quad (13)$$

Substitution of the experimentally determined values for $N_{\text{CH}_4}/N_{\text{CD}_4}$ and $N_{\text{CH}_3\text{CHO}}/N_{\text{CD}_3\text{CDO}}$, and an average value for $K_3^{\text{H}}/K_3^{\text{D}}$ of 1.43 (2) into eqn. 13, leads to an estimate of $k_8^{\text{H}}/k_8^{\text{D}} = 1.51$. 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 θ_{CH_3} and θ_{CD_3} is obtained very simply. Inspection of eqn. 4 shows that $\theta_{\text{CH}_3}/\theta_{\text{CD}_3} = N_{\text{CH}_3\text{CHO}}/N_{\text{CD}_3\text{CDO}}$, so that $\theta_{\text{CH}_3}/\theta_{\text{CD}_3} = 0.5$. 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 $\text{CH}_3(\text{CD}_3)$ 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 $\text{H}_2(\text{D}_2)$, reaction 3; and the inverse equilibrium isotope effect associated with the surface coverage by $\text{CH}_3(\text{CD}_3)$ 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 μ -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 $\text{Ru/Al}_2\text{O}_3$ 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 $\text{Ru/Al}_2\text{O}_3$ 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).

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

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/SiO₂ catalyst while methanol is the primary oxygenated product formed over the Ru/Al₂O₃ 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 Pt catalysts and by Ryndin et al. (26) for Pd catalysts. Unfortunately, the current understanding of the metal-support 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 exhibit a significant activity for the formation of oxygenated products from CO and H₂. For Ru/SiO₂ the principal product observed is acetaldehyde. The kinetics of acetaldehyde synthesis and the observation of an inverse H₂/D₂ 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 H₂/D₂ 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 γ -alumina, methanol is produced as the principal oxygenated species. This product readily decomposes back to CO and H₂ 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 μ -bridge-adsorbed CO to form a methoxy species. This group then undergoes reductive elimination to form methanol. The observation of an inverse H₂/D₂ 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/Al₂O₃ catalysts used for CO hydrogenation. For dispersions below 0.7, the specific activity for synthesis of methane and C₂₊ 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.

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 Ru/Al₂O₃ catalysts. In a more detailed study, King (4) reported that the specific activities of supported Ru catalysts for methanation and CO consumption decreased monotonically 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/Al₂O₃ 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, in situ infrared spectroscopy was used to characterize the structure of chemisorbed CO as a function of catalyst dispersion.

EXPERIMENTAL

Three γ -alumina-supported catalysts were used in this investigation. A 1.3% Ru/Al₂O₃ catalyst was prepared by adsorption of Ru₃(CO)₁₂ from pentane solution (5). The dried catalyst was reduced in flowing H₂ 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 H₂ chemisorption and determined to be 0.9. Two catalysts, a 3.0% Ru/Al₂O₃ and an 11% Ru/Al₂O₃ catalyst were prepared by incipient wetness impregnation of the support with an aqueous solution of RuCl₃, acidified to pH = 2 to suppress hydrolysis. 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% Ru/Al₂O₃ catalyst. The dispersion of the 3.0% Ru/Al₂O₃ catalyst, determined by H₂ chemisorption, was 0.5 and that of the 11% Ru/Al₂O₃ catalyst was 0.3.

Investigations of catalyst activity were conducted at 1 and 10 atm. The low 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 H₂ isotherms to be performed in the same cell. The flow of synthesis gas - a preblended H₂/CO mixture (H₂/CO = 2) - to the reactor was controlled by a needle valve 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 C₁ through C₅ range were separated using a 1 m x 2.4 mm stainless steel

column packed with Chromosorb 106. A 2.5 cm^3 sample was injected into the column maintained at 318K. The column temperature was then programmed to 478K at 10K/min. Separation of C_4 through C_{14} products was carried out using a 50 m x 0.25 mm fused silica, WCOT, column with SE-54 liquid phase. A modified Grob injection (6) was used to introduce the sample. With the column at 193K, a 10 cm^3 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 micro-reactor 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 Digilab FTS-10M Fourier Transform infrared spectrometer at a resolution of 4 cm^{-1} . Typically, 100 interfereograms, each acquired in 1.25 s, were co-added to improve the signal to noise ratio. 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/Al₂O₃ 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 H₂ isotherms. Approximately 800 mg of the catalyst was heated to 623K at 1K/min and then maintained at 623K for 2 hr. Following reduction, the cell was again evacuated and the temperature was reduced to 373K. An H₂ isotherm was then determined at 373K. Next, the cell was once more evacuated and, after reducing the temperature to 297K, a preblended H₂/CO mixture (H₂/CO = 2) was passed over the catalyst at 1 atm and 100 cm³/min (NTP) for 10 min. At the end of this time, the cell 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 H₂ 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 and reduction cycles were also carried out with a 50 mg sample of the 11% Ru/Al₂O₃ 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/Al₂O₃ catalyst, all of the data were collected using the 1.3% Ru/Al₂O₃ 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 $D_{Ru} < 0.75$ is significantly lower than the 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 C₂ through C₁₄ hydrocarbons increases in a manner similar to that observed for methane. In this figure, the

XBL 812-8028

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

XBL 812-7936

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 $n \geq 13$.

Figure 3 shows that the extent of deviation of the points for $n \geq 13$, 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 α is the probability of hydrocarbon chain growth (9,10). Table I shows that the magnitude of α increases slightly from 0.63 to 0.7 as the dispersion, measured after reaction, decreases from 0.82 to 0.67. Thereafter, α 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, $N_{C_n}/N_{C_{n-1}}$, 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.

XBL 812-7923

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

Table I. Effects of Dispersion on the Probability of Chain Growth^a

i	$D_{\text{Ru}}^{(i-1)^b}$	$D_{\text{Ru}}^{(i)^c}$	α
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 ^d	0.3	-	0.69

^aReaction Conditions: $T = 479\text{K}$; $P = 1 \text{ atm}$; $\text{H}_2/\text{CO} = 2$

Catalyst: 1.3% Ru/ Al_2O_3

^bMeasured before reaction cycle i

^cMeasured after reaction cycle i

^dCatalyst: 11% Ru/ Al_2O_3

XBL 812-7921

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/Al₂O₃ catalyst. The procedure used to obtain these spectra was as follows: A freshly prepared catalyst disc was reduced in situ in flowing H₂ at 573K and 10 atm for approximately 16 hr. The temperature was then reduced to 498K and a 3/1 H₂/CO mixture was fed to the reactor. Reaction was allowed to proceed for 10 min. During the last 2 min of this period 100 interferograms 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 H₂. 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 H₂ 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⁻¹ and two sharper bands located at 2040 and 1960 cm⁻¹. 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/Al₂O₃ catalyst: a) during reaction at 498K, 10 atm, H₂/CO = 3; b) following reduction in H₂ 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 H₂ at 573K for 12 hr.

Fig. 5.

XBL 812-7926

broad central band to mono-adsorbed CO (Ru-CO) and the bands at 2040 and 1960 cm^{-1} 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 H_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^{-1} .

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% Ru/ Al_2O_3 catalyst. Figure 6a illustrates the spectra obtained both under reaction conditions and following H_2 reduction. For the sake of comparison, spectra taken with the 1.3% Ru/ Al_2O_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^{-1} is

XBL 812-7919

Fig. 6. Infrared spectra obtained under reaction conditions and following reduction: a) 3.0% Ru/Al₂O₃; b) 1.3% Ru/Al₂O₃; Spectrum 1 is taken during reaction at 473K, 10 atm, H₂/CO = 3; Spectrum 2 is taken following reduction in H₂ 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^{-1} associated with di-adsorbed CO, are much less intense, though, for the 3.0% Ru/Al₂O₃ 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 data 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

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

where $D_{\text{Ru}}^{(i)}$ is the Ru dispersion and $A_{\text{M}}^{(i)}$ and $A_{\text{D}}^{(i)}$ 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_{C1} 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 points 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 planar 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 cor-

Table II. Effects of Dispersion on the Integrated Band Intensities for Adsorbed CO and the Activity for Methane Synthesis^a

i	⁽ⁱ⁾ b A _M	⁽ⁱ⁾ b A _D	⁽ⁱ⁾ A _M / (⁽ⁱ⁾ A _M + 0.5 ⁽ⁱ⁾ A _D)	r _{C₁} (s ⁻¹) ^c	D _{Ru} ⁽ⁱ⁾ d	N _{C₁} ⁽ⁱ⁾ (s ⁻¹)
1	4.20	2.25	0.79	2.25 x 10 ⁻⁴	0.80 ^e	2.81 x 10 ⁻⁴
2	3.00	2.00	0.75	4.00 x 10 ⁻⁴	0.60	6.67 x 10 ⁻⁴
3	2.85	1.60	0.78	5.29 x 10 ⁻⁴	0.55	9.62 x 10 ⁻⁴
4	n.a.	n.a.	-	6.14 x 10 ⁻⁴	-	-
5	2.35	1.45	0.76	6.9 x 10 ⁻⁴	0.46	15.1 x 10 ⁻⁴
6	2.18	1.47	0.75	6.96 x 10 ⁻⁴	0.44	15.8 x 10 ⁻⁴
7	2.18	1.37	0.77	7.19 x 10 ⁻⁴	0.43	16.7 x 10 ⁻⁴
8	1.88	0.70	0.84	7.75 x 10 ⁻⁴	0.34	22.8 x 10 ⁻⁴

^aCatalyst - 1.3% Ru/Al₂O₃; T = 498K; P = 10 atm; H₂/CO = 3

^bArbitrary units

^cBased on total number of Ru atoms

^dFrom eqn. 1

^eAssumed

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

^fFollowing exposure to 2.5 atm CO at 473K for 8 hr and subsequent reduction in H₂ at 10 atm and 573K for 12 hr

responding to $0.3 > D_{\text{Ru}} > 0.75$, the fraction of sites associated with planer surfaces decreases 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 $D_{\text{Ru}} = 0$ and $D_{\text{Ru}} = 0.75$. 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 consistency.

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 $D_{\text{Ru}} < 0.5$. 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, α , 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 metal-support 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 π^* -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 π^* 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 α 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_1 units. Deviation of the point for C_2 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 C_{12+} 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 C_{12+} 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_2O_3 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_2O_3 catalyst sinters under reaction conditions, the fraction of mono-adsorbed 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 di-adsorbed CO, while maintaining a nearly constant ratio of the two adsorbate forms. It is conceivable 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 nor 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. In situ 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 micro-reactor, an infrared reactor, and gas chromatographs 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 valves and is measured by monitoring the pressure drop produced across a fixed capillary tube. Provisions are also available for injecting 1 cm³ aliquots of a particular component into a steady flow going to the reactor.

The gases used for the majority of the reaction studies are H₂ (LBL, > 99.999%), He (LBL, > 99.995%), and CO (Matheson UHP, > 99.8%). Preblended H₂/CO mixtures prepared and analysed in the laboratory are also used. Ethylene (Matheson CP, > 99.5%) and D₂ (LBL, > 97.5%) have also been used on occasion as components of the synthesis gas feed. Helium and H₂/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 H₂ is passed through a Matheson Deoxo unit to remove oxygen.

The use of preblended H₂/CO mixtures insures that gas compositions are accurate and consistent for all runs. Mixtures are prepared by

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

sequential 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_2 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 Swagelok 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 1K.

Infrared Reactor

A schematic of the cell utilized for in situ 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 $\pm 1\text{K}$ of the desired value; however due to the possibility of infrared and radiant 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

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

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_2 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_2 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 in situ 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 5×10^7 to 5×10^8 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. Cracks 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 chromatograph 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 chromatograph 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 chromatograph. 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 chromatograph. 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 Perkin-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 α -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_8 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.

Instrument: Perkin-Elmer Sigma 3b
 Column: fused silica SE-54 WCOT capillary
 Carrier Gas: He; P = 270 kPa; split ratio = 20:1
 Detector: FID
 Sample: modified Grob injection, 10 ml gastight syringe
 Temperature Program: initial temp: 193K
 time: 5 min
 temp ramp: 5K/min
 final temp: 473K

Fig. 3. Sample chromatogram obtained with capillary column.

APPENDIX II

Chemisorption-Apparatus and Procedures

Apparatus

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_2 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 O_2 and through a molecular sieve trap cooled to 78K for removal of H_2O . 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.

Volumetric Adsorption Apparatus

1. Mechanical Pump
2. Oil Diffusion Pump
3. Liquid N₂ Cooled Trap
4. Bayard-Alpert Gage
5. Baracel Pressure Transducer
6. Adsorption Cell
7. Furnace
8. Ultra-Torr Fittings
9. Calibrated Volume
10. 3-Way Glass Stopcocks
11. Purifier, DEOXO
12. Molecular Sieve Trap, 78K
13. Molecular Sieve Trap

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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_2O . 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 2×10^{-3} 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 5×10^{-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.

Adsorption Isotherm: Sample Calculation

Catalyst: 3.0% Ru/Al₂O₃

Weight: 1.53 g

Adsorbate: H₂

Adsorption temperature: 378K

Dosing volume: V₁=32.4 cm³, T₁=298KAdsorption cell: effective volume, V₂=21.7 cm³, T₂=378KH₂ Molar Uptake Data

i	Pressure (torr)			<u>H₂ uptake x 10⁵ (moles)</u>	
	P _i	P _{exp<i>i</i>-1}	P _{exp<i>i</i>}	n _i	n _i
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 dosing volume prior to admitting to catalyst cellP_{exp*i*} = equilibrium pressure following ith aliquotn_i = molar uptake for the ith aliquot^(a)

(a) from ideal gas law

$$n_i = \frac{P_i V_1}{RT_1} + \frac{P_{exp_{i-1}} V_2}{RT_2} - \frac{P_{exp_i}}{K}$$

$$K = \frac{R T_1 T_2}{V_1 T_1 + V_2 T_2}$$

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Fig. 2. Sample H₂ and CO adsorption isotherms.

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