The Role of Alkali Metals as Promoters in the Methanation and Fischer–Tropsch Reaction: An *in Situ* Study

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The effect of alkali metals as catalytic modifiers on the methanation and Fischer–Tropsch reaction over a series of silica-supported Ru catalysts has been studied. When hydrocarbon product distributions were compared at constant CO conversion or at constant CH_4 formation turnover frequencies, rather than at constant temperature, differences in selectivity were small for the series of catalysts studied. The temperature-programmed desorption of CO from these catalysts showed the presence of three desorption maxima, centered at 100, 220, and 450°C, respectively. The relative intensity of the maximum centered at 220°C was observed to increase slightly on the catalysts modified by the addition of alkali metals. However, this slight increase in binding energy did not appear to promote the formation of surface carbon. The high-temperature maximum centered at 450°C was assigned to CO formed by the reaction between surface carbon and H_2O from the support. An "*in situ*" infrared study of the CO surface species present on the catalyst surface during reaction showed only one band centered at 2030 cm^{-1} on supported Ru. This was in contrast to the two bands centered at 2020 and 1950 cm^{-1}, which were observed for the K- and Cs-promoted catalysts. The results of this study suggest a depression in the rate of hydrogenation of the surface carbon species as a result of the addition of the alkali metal modifier. This is explained by invoking site blocking by the alkali metal adatoms rather than by an electronic effect.

INTRODUCTION

The use of alkali metals as catalytic modifiers for many important industrial catalytic processes has been a part of catalytic technology for many years (*1, 2*). However, the role played by alkali metals, either as selective poisons or as catalytic promoters for group VIII transition metals, is still not fully understood and is presently a subject of intense debate (*3–12*). By far the most attractive theory is that the alkali metal atoms modify the local electron density of the transition metal either directly (*8, 13–16*) or through the support (*3*).

Recently, Ertl *et al.* (*15*) have performed a detailed study on the role of potassium in the catalytic synthesis of ammonia over Fe. They find that K strongly segregates to the surface, forming a submonolayer of adsorbed K and O having a stoichiometric ratio of unity. Because this K–O adlayer has a net dipole moment in the direction of the surface, they conclude that the net result is an enrichment in the electron density at the alkali metal adlayer–Fe interface. In the case of the ammonia synthesis this enhanced electron density of the Fe atoms decreases the surface coverage of ammonia, which is chemisorbed through the lone pair of electrons on the nitrogen atoms. At the same time, back-donation of electrons into the antibonding orbitals of N_2 results in an increase in the dissociative adsorption of N_2, which is the rate-limiting step in the ammonia synthesis.

A similar but somewhat more general explanation of the electronic nature of the promotional effect of alkali metal atoms has recently been suggested by Shyu *et al.* (*17*). If one applies this same line of reasoning to the methanation reaction and the closely related Fischer–Tropsch synthesis, one should conclude that the enhanced back-donation of electrons from the transition metal atom to the antibonding orbitals of

adsorbed CO should result in a weakening of the CO bond. However, it is important to point out that a weakening in the strength of the CO bond does not necessarily result in CO dissociation. Crowell et al. (18) have observed enormous red shifts in the position of the CO stretching frequency (>700 cm^{-1}) on potassium-modified Pt and Rh single crystals. Only in the case of Rh was CO dissociation observed.

Group VIII transition metals which are capable of promoting the dissociation of CO under reaction conditions are, in general, good methanation and Fischer–Tropsch catalysts. The addition of an alkali metal modifier capable of promoting the dissociative adsorption of CO should, therefore, improve the catalytic activity of the group VIII metal for these reactions. However, methanation and Fischer–Tropsch studies on both well-defined single crystals (16) and on supported metals (2, 11, 12), with one important exception (5), overwhelmingly show that the rate of both reactions is strongly depressed by the addition of an alkali metal. In addition to this observation, the nature of the alkali metal precursor appears to make little difference. For example, K atoms added to a well-defined Ni single-crystal surface (8, 16) have virtually the same effect on the methanation and Fischer–Tropsch reaction rate as does a supported Ru–K/SiO$_2$ catalyst prepared by the coimpregnation of SiO$_2$ using a solution which contains RuCl$_3$ and KNO$_3$ (11). Additionally, it makes very little difference whether the K is added as KNO$_3$, KCl, K$_2$CO$_3$, or KOH (2, 7, 11). Still more puzzling is the effect of added sulfur or phosphorous. Because alkali metals are electron donors, the effect should be reversed through the addition of electron-withdrawing atoms. The careful work of Goodman shows that this is not the case (8, 16).

The role of sulfur as a poison appears to be considerably more severe than that of either phosphorous (16) or potassium (8). The role of a modifier such as an alkali metal adatom can be readily understood in terms of its properties as an electron donor (14). Because CO bond cleavage leads to the formation of surface carbon, carbon buildup on the surface of the catalyst will occur when either the rate of CO bond cleavage is increased or when the rate of hydrogenation of this surface carbon is decreased. There is general agreement that carbon buildup does occur as the result of the addition of alkali metal modifiers and that this increase in the steady-state carbon layer depresses the methanation rate to a greater extent than it does the rate of formation of higher hydrocarbons and olefins (8, 16). The role of the alkali metal additives should therefore be more appropriately discussed in terms of selective poisons rather than promoters.

In general, hydrocarbon product distributions resulting from the CO–H$_2$ reaction over metal catalysts modified by the addition of alkali metals have been compared at constant temperature (11). Because CO conversions are higher over the unpromoted catalysts, one would expect hydrocarbon product distributions over these catalysts to be significantly skewed toward methane and saturated hydrocarbons. The purpose of this study is to assess the underlying reasons for carbon formation. We have therefore compared hydrocarbon distributions under conditions of (1) constant temperature, (2) constant CO conversion, and (3) constant rate of methane formation. In addition to these studies, we have used a series of "in situ" surface characterization techniques to obtain a better understanding of the factors (electronic or otherwise) which lead to a modification of the steady-state carbon overlayer.

EXPERIMENTAL

Apparatus. A conventional flow system which enables use of a reactor as either a pulse microreactor or as a single-pass differential reactor was used. The construction of this flow system, except for minor modifications, has been described in a previous report (11, 19). The microreactor

used in both the temperature-programmed desorption studies (TPD) and the steady-state reaction rate studies was constructed from 12-mm Pyrex glass tubing and had a total volume of 4 ml. The catalyst was held in place by means of a fritted ceramic disk and quartz wool. The reactor was externally heated using an oven connected to a variable temperature programmer (Valley Forge Model PC-6000). For the acquisition of TPD data, a Gow-Mac gas chromatograph (Model 550P) equipped with a thermal conductivity detector was used. A 1-m Carbosieve-S column was found to be adequate for performing the necessary analytical separations. More precise hydrocarbon product distributions were obtained using a Hewlett–Packard (Model HP5880A) programmable gas chromatograph equipped with a flame ionization detector. Hydrocarbon separation was performed using a 3-m Chromosorb 106 column operated in a temperature-programmed mode between 60 and 190°C.

For the infrared spectral studies, a cell, also capable of being operated either as a pulse microreactor or as a single-pass differential reactor, was used. The cell was designed in such a way that reactant gases were forced through a sample disk with little or no leakage around the edges. Details regarding its construction have been published elsewhere (19). Infrared spectra were obtained using a Perkin–Elmer Model 281 infrared spectrophotometer, interfaced with a Perkin–Elmer Data Station in order to facilitate handling of the data.

Materials. The gases used in this study were subjected to the following purification treatment: He (Cranston Welding, 99.995%) was first passed through a molecular sieve trap maintained at −196°C, and then through a Supelco carrier gas purifier to remove O_2 and H_2O. An MnO trap backed by a second molecular sieve cooled to −196°C was then used to reduce O_2 and N_2 concentrations in the carrier gas to the ppb range. CO (Cranston Welding, research grade) was purified by passing it through an Analabs molecular sieve trap cooled by an isopropanol/liq N_2 slush bath. This was followed by an MnO trap. For the Fischer–Tropsch studies, it was convenient to use a premixed H_2/CO reaction gas mixture (Cranston Welding) having a ratio of 3 : 1. It was not subjected to any further purification.

The silica-supported samples used in this study were prepared by impregnation or coimpregnation. The appropriate weight of $RuCl_3 \cdot 3H_2O$ (Strem Chemical) and alkali promoter nitrate salt (Pfaltz & Bauer) were dissolved in deionized water sufficient to completely wet the support (Cab-O-Sil, M-5, Cabot Corp.). The resultant slurry was dried at room temperature for several days and stirred at regular intervals to retain uniformity. The dried catalyst was ground and sieved before use.

The Ru metal loading was 0.3 mmol/g of support or 3 wt% Ru. The metal alkali/Ru mole ratio was 0.1 for all of the catalysts studied. Three different preparations for the Ru–K/SiO₂ were used. These preparations differed only in the sequence in which the impregnation was carried out. Ru–K/SiO₂ denotes a catalyst prepared by coimpregnation. Ru*–K/SiO₂ denotes a preparative sequence in which the Ru was added first, followed by drying and impregnation with a KNO₃ solution; Ru–K*. SiO₂ denotes the reverse sequence.

Procedure. Catalyst pretreatment was as follows: Each catalyst sample (ca. 300 mg) was heated in flowing He (25 ml/min) from 25 to 130°C and maintained at 130°C for 1 hr. The temperature was then increased from 130 to 450°C in flowing H_2 (25 ml/min) and heated in flowing H_2 for 2 hr. The sample was then heated in flowing He for 1 hr at 460°C, followed by cooling to room temperature in He.

Adsorption measurements were performed with the associated flow system arranged to operate in the pulse mode. Measured volumes (97 μl) of CO were pulsed through the catalyst bed until the height of successively eluted peaks was identical.

The 1-m Carbosieve-S column used for analysis was maintained at 140°C. The temperature-programmed desorption studies were performed by increasing the temperature of the catalyst at a rate of 10°C/min in flowing He (25 ml/min). Samples for analysis were taken at 4-min intervals, and the amounts of CO and CO$_2$ were measured by gas chromatography.

Two series of Fischer–Tropsch studies were performed. In the first series the H$_2$–CO mixture was reacted over the catalyst at the desired reaction temperature for 20–30 min. A sample was taken for analysis, and the catalyst was then flushed in H$_2$ for 20 min. The procedure was similar to that used by Vannice (20). Conversions varied from 2% on some of the alkali-promoted catalysts to 15% on the unpromoted Ru catalyst. The thermal conductivity detector on the Gow-Mac gas chromatograph enabled adequate paraffin–olefin separation through C$_3$. These data were collected over the (160–240°C) temperature range. This enabled the calculation of activation energies.

In order to compare the different promoted catalysts under conditions of constant CO conversion and constant CH$_4$ turnover frequency, a fully computerized Hewlett–Packard gas chromatography equipped with FID detection was used. Hydrocarbon products through C$_6$ were ade-

quately resolved. Blank experiments on K/SiO$_2$ and pure SiO$_2$ were also performed.

RESULTS

Hydrocarbon product distribution studies. Hydrocarbon distributions obtained at 220°C for the unpromoted and the alkali-promoted Ru/SiO$_2$ catalysts are shown in Table 1. CO conversion was 15% for the unpromoted Ru catalyst and about 2% for Ru–Cs/SiO$_2$, the most inactive catalyst studied. The most striking difference between the promoted and unpromoted catalysts was the increase in the olefin yield. The C$_2^{2-}$/C$_2^-$ ratio increased by nearly two orders of magnitude from Ru/SiO$_2$ to Ru–Cs/SiO$_2$, and the C$_3^{2-}$/C$_3^-$ ratio increased by about one order of magnitude for the same series of catalysts. The increase in the yield of the higher-molecular-weight hydrocarbons obtained on the promoted catalysts is shown in the bar graph (Fig. 1). It is important to note that the different preparative treatments for the series of Ru–K/SiO$_2$ catalysts had little effect on both the hydrocarbon distribution and the steady-state reaction rate.

Because CO conversions can have a relatively large effect on hydrocarbon product distributions, a second comparative study was performed in which CO conversions were kept constant. In this study the tem-

TABLE 1

Hydrocarbon Selectivities at 220°C over Alkali Promoted Ru/SiO$_2$ Catalysts

Catalyst	C$_2^{2-}$/C$_2^-$	C$_3^{2-}$/C$_3^-$	C$_2$/C$_3$	Dispersion %	Conversion (% CO conver.)	Turnover frequency $\times 10^3$ (molec CH$_4$/site · sec)
Ru/SiO$_2$	0.03	0.34	1.3	12.5	15	5.78
Ru–Li/SiO$_2$	0.26	1.60	0.62	13.7	2.5	1.32
Ru–Na/SiO$_2$	0.17	2.8	0.82	17.1	2.2	1.15
Ru–K/SiO$_2$[a]	0.82	6.2	0.72	11.1	1.9	0.73
Ru*–K/SiO$_2$[b]	0.97	5.1	0.73	~11	1.9	0.63
Ru–K*/SiO$_2$[c]	0.85	4.9	0.72	~11	1.9	0.74
Ru–Cs/SiO$_2$	1.90	7.1	0.74	13.4	1.7	0.52

Note. Metal loading, 0.3 mmol of Ru/g of catalyst; alkali metal/Ru = 0.1; flow rate 25 ml/min; H$_2$/CO = 3.
[a] Catalyst prepared by coimpregnation.
[b] Denotes impregnation with Ru first.
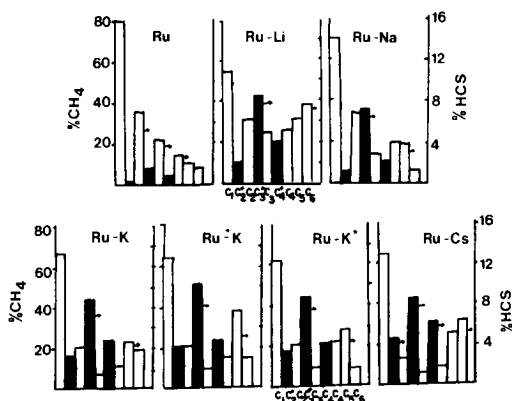[c] Denotes impregnation with K first.

FIG. 1. Hydrocarbon distribution at 220°C. Darkened bars denote olefins.

perature was adjusted to give a CO conversion which was approximately equal to 2%. The results, displayed in Table 2, show that differences between unpromoted and promoted catalysts were much smaller than those obtained at constant temperature. For the series of catalysts studied, C_2^{2-}/C_3^- ratios differed by less than one order of magnitude, and C_3^{2-}/C_3^- ratios, by a factor of about 3. The temperature required to obtain a 2% conversion of CO was observed to increase from 184°C on the unpromoted Ru/SiO$_2$ catalyst to 225°C on the Ru–Cs/SiO$_2$ catalyst. To assess the influence on cationic charge as a possible catalytic modifier, a Ru–Ca/SiO$_2$ catalyst was also studied. Product distributions and activation ener-

gies for methane formation for the Ru/SiO$_2$ and Ru–Ca/SiO$_2$ catalysts were virtually identical, strongly suggesting that Ca tends to segregate to the support. This is in good agreement with the recent results of Ertl (21).

A third hydrocarbon product distribution was obtained under conditions in which the temperature was adjusted to insure a constant turnover frequency for the rate of formation of CH$_4$. In this way, hydrocarbon product distributions could be compared under conditions for which the rate of the hydrogenation of the surface species containing carbon were approximately constant. Because these conditions corresponded quite closely to those obtained at constant CO conversion, the two sets of data were quite similar. The results are shown in Table 3. Higher product hydrocarbon yields are displayed in the bar graph in Fig. 2. C_2^{2-}/C_2^- and C_3^{2-}/C_3^- ratios, with the exception of the Ru–Cs/SiO$_2$ catalyst, differed by a factor which was between 2 and 3. From these data it is apparent that the very large differences in hydrocarbon selectivity observed under conditions of constant temperature are markedly reduced when hydrocarbon distributions are compared, either at constant CO conversion or at constant surface carbon hydrogenation rate.

Temperature-programmed   desorption

TABLE 2

Hydrocarbon Selectivities at Constant CO Conversion over Alkali-Promoted Ru/SiO$_2$ Catalysts

Catalyst	Temp. (°C)	C_2^{2-}/C_2^-	C_3^{2-}/C_3	C_2/C_3	Conversion %	Dispersion[a] %	E_A (C$_3$) (kJ/mol)	E_A (CH$_4$) (kJ/mol)
Ru/SiO$_2$	184	0.3	2.6	0.2	2.5	12.5	101 ± 10	132 ± 5
Ru–Li/SiO$_2$	214	0.6	4.8	0.3	2.0	13.7	130	138
Ru–Na/SiO$_2$	215	0.4	2.7	0.3	1.9	17.1	104	125
Ru–K/SiO$_2$	220	1.0	4.7	0.6	1.9	11.1	121	123
Ru–Rb/SiO$_2$	221	1.5	6.7	0.5	1.8	13.5	102	115
Ru–Cs/SiO$_2$	225	2.3	9.2	0.2	2.0	13.4	115	118
Ru–Ca/SiO$_2$	202	0.2	4.5	0.5	1.8	10.2	—	132

Note. Reaction conditions and metal loadings were identical to those in Table 1.

[a] Measured using CO adsorption.

TABLE 3

Hydrocarbon Selectivities at Constant CH$_4$ Turnover Frequencies over Alkali-Promoted Ru/SiO$_2$ Catalysts

Catalyst	Temp. (°C)	C$_2^=$/C$_2$	C$_3^=$/C$_3^-$	C$_2$/C$_3$	Disp. (%)	Turnover frequency ×10^3 (molec. CH$_4$/site · sec)
Ru/SiO$_2$	185	0.29	2.2	0.53	12.5	0.60
Ru–Li/SiO$_2$	209	0.65	4.6	0.53	13.7	0.53
Ru–Na/SiO$_2$	215	0.32	3.7	0.71	17.1	0.67
Ru–K/SiO$_2^a$	219	0.95	6.8	0.73	11.1	0.64
Ru*–K/SiO$_2^b$	220	0.97	5.1	0.73	~11	0.63
Ru–K*/SiO$_2^c$	218	0.94	5.4	0.68	~11	0.65
Ru–Cs/SiO$_2$	221	2.10	6.4	0.74	13.4	0.50

Note. Reaction conditions and metal loadings were identical to those in Table 1.
[a] Catalyst prepared by coimpregnation.
[b] Denotes impregnation with Ru first.
[c] Denotes impregnation with K first.

studies. In order to determine whether CO was more strongly adsorbed on the alkali-promoted catalysts, a series of TPD studies were performed. In addition to information regarding CO binding energies, TPD chromatograms are also useful in probing the catalytic activity of each catalyst for the formation of surface carbon as a result of the disproportionation of CO (Boudouard Reaction). In these studies, desorption was initiated starting with a monolayer of adsorbed CO. Because desorption–readsorption must be taken into account in TPD studies on porous catalysts, metal dispersions must be considered (22–24). The net effect of increasing the metal dispersion is to increase the extent of desorption–readsorption by virtue of the larger number of adsorption sites. This, in turn, has the effect of lengthening the catalyst bed with an apparent increase in the high-temperature desorption maximum. The results of this study, for a series of four catalysts, are shown in Fig. 3. Metal dispersions for all
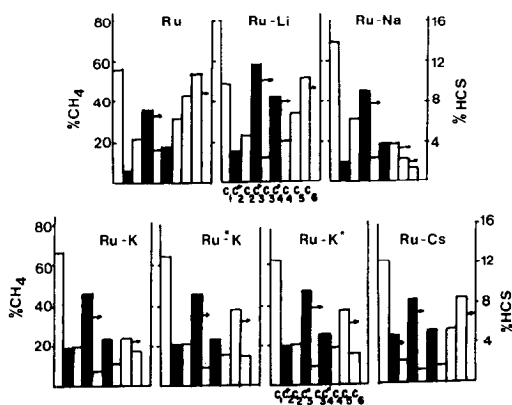

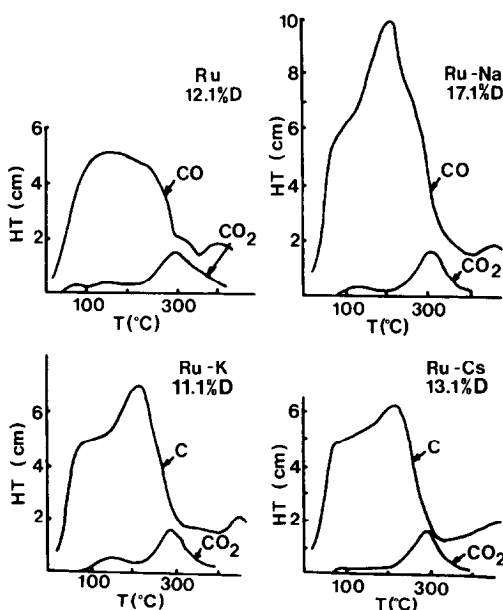FIG. 2. Hydrocarbon distribution at constant CO conversion. Darkened bars denote olefins.

FIG. 3. Temperature-programmed desorption chromatograms for Ru/SiO$_2$, Ru–Na/SiO$_2$, Ru–K/SiO$_2$, Ru–Cs/SiO$_2$. Metal dispersions are shown. Temperature was increased linearly at 10°C/min.

catalysts are included in the figure. Three CO desorption maxima, centered at 100, 220, and 450°C, respectively, were observed for both the promoted and the unpromoted catalysts. The intensity of the two low-temperature desorption maxima was reversed as a result of the addition of the alkali metal promoter. However, the change in the binding states of CO as a result of this promotional effect was not large. The much larger intensity of the high-temperature desorption maximum observed for the Ru–Na/SiO$_2$ catalyst can be explained by considering the higher metal dispersion obtained for this catalyst. The desorption maximum at 450°C is due to the reaction between surface carbon either on the Ru or on the support, and H$_2$O from the support, rather than to a high-temperature CO binding state. This was determined by performing an "in situ" TPD experiment using infrared spectroscopy. In this experiment the infrared spectrum of adsorbed CO was continually scanned as the desorption products were monitored. The results, shown in Fig. 4, indicate that there was no infrared active CO left on the surface at temperatures in excess of 300°C. We conclude, therefore, that the high-temperature desorption maximum probably occurs as the result of a reaction between surface carbon (from the Boudouard Reaction) and H$_2$O from the support. Attempts to reduce the amount of high-temperature CO by
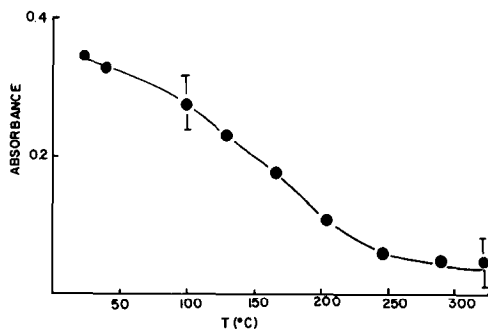

FIG. 5. Sequential temperature-programmed desorption chromatograms for Ru–K/SiO$_2$.

treatment in He at 460°C, following reduction in H$_2$ at 450°C, were unsuccessful. Higher dehydroxylation temperatures were not attempted for fear of damaging the Pyrex microreactor and ceramic fritted disks used in this study. The relatively low levels of H$_2$ which would be produced as a result of the reaction between H$_2$O and surface carbon could not be detected by gas chromatography. For this reason, the desorption of a CO species which is infrared inactive could not be completely ruled out. The integrated area under the TPD CO$_2$ curve was, within experimental error, virtually identical for all of the catalysts studied. We therefore conclude that the role of the alkali metal modifier was not to promote the formation of additional surface carbon.

Because reaction rates on the alkali-promoted catalysts underwent a rather lengthy deactivation prior to the attainment of a steady-state reaction rate, we considered the possibility that additional buildup of surface carbon could occur as the result of catalyst aging. A series of four successive TPD runs (Fig. 5) confirmed this suspicion. Following each TPD run the catalyst was rereduced according to the standard pre-

FIG. 4. Absorbance of CO vs temperature obtained during the temperature-programmed desorption of CO on Ru–Na/SiO$_2$. Temperature was increased linearly at 10°C/min.
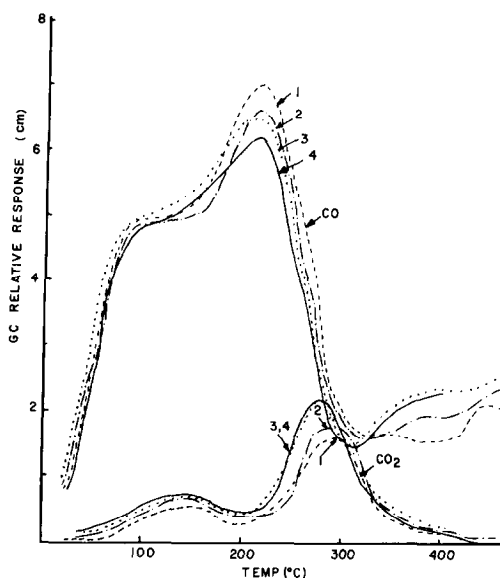
treatment schedule. In each successive run the area under the CO_2 curve was observed to increase slightly. After the fourth TPD run the amount of CO_2 formed in subsequent runs was constant. This increase in the amount of surface carbon was concomitant with an increase in CO formed as a result of the reaction between surface carbon and H_2O. This could readily be seen by observing the increase in the intensity of the high-temperature desorption maximum centered at 450°C. Additionally, the increase in the amount of surface carbon appears to occur at the expense of the more strongly bound CO. CO chemisorption measurements revealed no changes in the Ru metal dispersion as the result of each successive TPD run. The rather lengthy deactivation in reaction rate observed on the alkali-promoted catalysts was not observed on the unpromoted Ru/SiO_2 catalysts.

Infrared studies. In order to probe the structure of the CO species adsorbed on the catalyst surface during reaction, and to understand the nature of the perturbation induced by the presence of the alkali metal, a series of *"in situ"* infrared spectra were recorded. These spectra, which were re-corded at 220°C, are shown in Fig. 6. In the case of the unpromoted Ru/SiO_2 catalyst only one rather intense symmetrical band, centered at 2038 cm^{-1}, was observed. This absorption band, which is due to CO adsorbed in the linear configuration, is consistent with previous infrared studies on the adsorption of CO on well-reduced Ru (*11*). The addition of an alkali metal promoter results in a considerable broadening of this band to the low-frequency side, with the concomitant development of a feature centered at about 1950 cm^{-1}. The asymmetry was most noticeable for the Ru–K/SiO_2 and the Ru–Cs/SiO_2 catalysts. It is well known that infrared bands due to CO adsorbed in the linear configuration generally have infrared stretching frequencies which are centered above 2000 cm^{-1}. On the other hand, CO molecules which are multicoordinated to the surface have infrared stretching frequencies which are centered below 2000 cm^{-1} (*25*). Although the main feature in the infrared spectrum of the alkali-modified Ru catalysts still occurs above 2000 cm^{-1}, and is indicative of linearly bound CO, the noticeable broadening of the infra-red band coupled with the feature at 1950
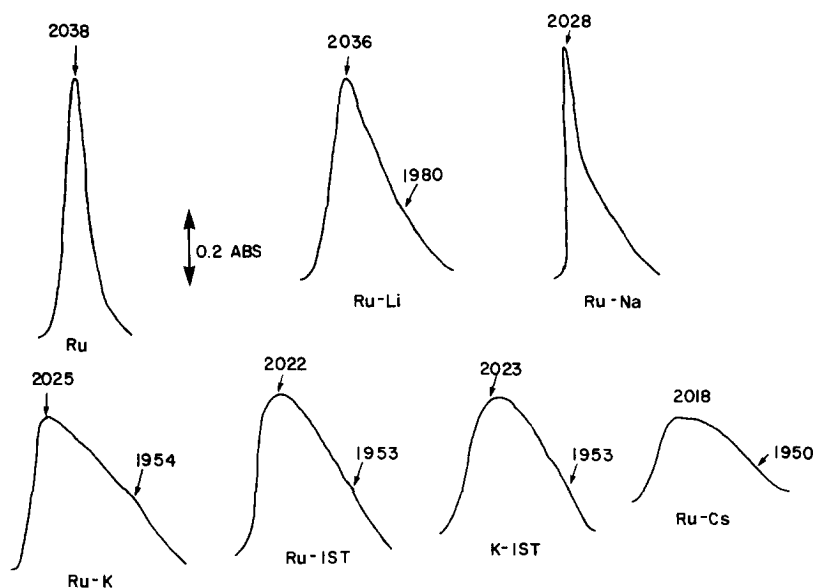

FIG. 6. *"In situ"* infrared spectra at 220°C.

cm^{-1} suggests that some multicoordinated CO is present.

DISCUSSION

The results of this study suggest that the binding states of CO are not greatly changed as the result of the addition of the alkali metal promoters. The TPD studies do suggest some increase in the binding energy of CO, in agreement with previous studies, performed both in this laboratory (*11*) and elsewhere (*17*). This rather modest increase in binding energy is suggestive of a mild electronic effect brought about by an increase in the electronic density at the transition metal site. The net result of this increase in electron density is to increase the extent of back-donation, thereby increasing the strength of the carbon–metal bond, while at the same time decreasing the strength of the carbon–oxygen bond. The "*in situ*" infrared results are in agreement with this interpretation. The position of the infrared band due to the CO stretching vibration was observed to decrease from 2038 cm^{-1} on the unpromoted Ru/SiO_2 catalyst, suggesting a weakening in the strength of the CO bond. However, one must be careful in carrying this electronic interpretation too far, as there are several effects which tend to muddy the waters. The chemical state of the modifier cannot be precisely determined. The most convincing study to date is that performed by Ertl and co-workers on synthetic Fe ammonia catalysts (*15, 21*). These authors, on the basis of electron microscopy, work function measurements, and TPD studies of the potassium adlayer, have suggested an adsorbed K–O configuration having a K/O stoichiometric ratio of one. When this configuration is invoked, or when alkali metal atoms are added to well-defined transition metal crystal planes, as in the very elegant work of Goodman (*8, 16*) and Crowell *et al.* (*18*), electron donation to the antibonding orbitals of CO is easily understood. On the other hand, Goodman and

Kiskinova (*16*) have also shown that the nature of the adatom, with the exception of S, appears to make little difference. Additionally, the nature of the alkali metal salt used to modify the catalytic activity of a supported group VIII metal appears to make little difference (*7, 11, 17*).

The electron donor properties of K–O can be understood in terms of the model proposed by Ertl *et al.* (*15, 21*). However, the electron donor properties of such modifiers as KCl and NaCl are less clear. The red shifts observed in this study can also be explained by considering a decoupling of the CO dipole–dipole interactions by virtue of the disruption in the periodicity of the adlayer induced by the presence of the alkali metal adatoms. In fact, because the red shifts observed are relatively small and because carbon formation is not enhanced on the alkali-modified catalysts, we favor this interpretation. If the carbon–oxygen bond in CO were significantly weakened as the result of electron back-donation, an increase in the rate of CO disproportionation would be expected on the alkali-modified catalysts. The relatively constant area under the CO_2 curve in the TPD studies suggests that carbon formation is not enhanced. Because of this result, we suggest that the increase in the carbon overlayer is not caused by a significant increase in the rate of the Boudouard Reaction on account of an electronic effect induced by the presence of the alkali metal, but by a decrease in the rate at which the hydrogenation of the surface carbon species occurs.

Because the methanation reaction is more hydrogen demanding than the Fischer–Tropsch reaction, its rate is more strongly depressed than the rate of formation of the Fischer–Tropsch products. This results in the selective poisoning of the methanation reaction. When the turnover frequency for methane formation is maintained constant (Table 3 and Fig. 2), variations in hydrocarbon distributions are greatly reduced. Under these conditions, the rate of the hydrogenation step can be

assumed to be approximately constant for the series of catalysts studied.

A comparison of product selectivities at different temperatures is strictly valid only for cases in which the activation energy for all of the steps in a given kinetic sequence are the same for both the alkali-modified and the unmodified catalysts. It is not, of course, possible to obtain activation energies for each step in the kinetic sequence. However, the apparent overall activation energy for methane formation and for C_3 hydrocarbon formation (Table 2) suggests that differences in activation energies for both the methanation reaction and the Fischer–Tropsch reaction are not more than 10 kJ/mol when the experimental error in the measurements is taken into account. These rather small differences in activation energy may very well have resulted in small but measurable changes in the olefin/paraffin ratios at constant turnover frequency or at constant conversion. However, it would be rather difficult to reconcile the very large orders of magnitude differences in paraffin/olefin ratios observed at constant temperature with these small differences in activation energies. Because carbon formation is not significantly affected by the alkali metal modification, we conclude that the poisoning of the rate of the hydrogenation step is a more likely cause. It is therefore of interest to consider the hydrogenation step in more detail. Two possibilities exist: (1) the effect of the alkali metal modifier is to reduce the availability of hydrogen on the surface; or (2) the role of the alkali metal is to modify the rate at which hydrogen adds to the carbon atoms on the surface, as the result of an ensemble effect.

Hydrogen chemisorption measurements performed under static conditions suggest that hydrogen adsorption is depressed on the catalysts modified by the addition of alkali metals (17). However, extrapolation of static chemisorption measurements performed at 25°C to dynamic hydrogen chemisorption, which occurs during reaction at temperatures in excess of 200°C, is not war-

ranted. In a previous study Miura et al. (26) addressed this question by considering the coadsorption of H_2 and CO under reaction conditions. In that study, a strong surface interaction between adsorbed hydrogen and adsorbed CO was observed; moreover, the CO–H adlayer was not significantly perturbed by the presence of alkali modifiers.

The possibility that an electronic effect may play an important role in depressing hydrogen chemisorption can also be considered in light of a previous experiment, also performed in this laboratory. Miura and Gonzalez (27) performed a methanation and Fischer–Tropsch study on a series of well-defined Pt–Ru/SiO₂ bimetallic clusters. The turnover frequency for methane formation on Pt at 220°C is about two orders of magnitude lower than that on Ru. For this reason, Pt can be considered to be catalytically inactive for this reaction and to be acting merely as a surface diluent. Turnover frequencies for methane formation as a function of surface composition were taken from Table 2 of Ref. (27) and are replotted in Fig. 7. The straight line represents turnover frequencies calculated on the basis of a facile reaction. The results show that the reaction is far from being facile. When the surface Ru/Pt ratio drops to between 4 and 5, there is a sharp decline in the rate of the methanation reaction. This is
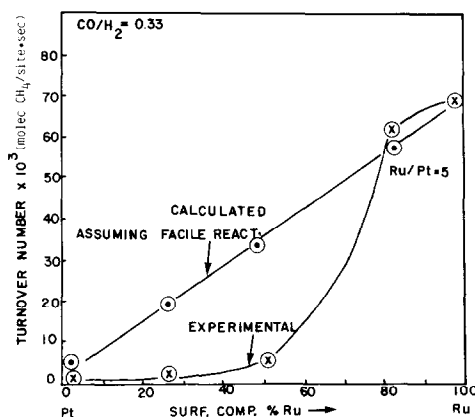
FIG. 7. Activity for CH_4 formation as a function of surface composition at 220°C. Data from Table 2, Ref. (27).

in all likelihood not due to an electronic effect induced by Pt. After all, Pt is an excellent hydrogenation catalyst and should, if anything, increase the concentration of hydrogen atoms on the surface.

The results are suggestive of an ensemble effect rather than an electronic effect. The requirement of an ensemble consisting of approximately 4 adjacent Ru atoms has been duplicated in a recent unpublished methanation study on well-characterized silica-supported Rh–Ru bimetallic clusters (28). These results are in striking agreement with the proton-induced reduction of CO to CH_4 on a series of homonuclear and heteronuclear metal carbonyls (29). These authors showed that a minimum cluster size of 4 active metal atoms was required to catalyze the formation of CH_4. For the reaction between $[Fe_4(CO)_{13}]^{2-}$ and HSO_3CF_3, Whitmire and Shriver (30) identified an intermediate consisting of a carbon atom bound to 4 Fe atoms in a "butterfly" configuration. The ensemble requirement of 4 appears to have an analog in the homogeneous reaction between polynuclear transition metal carbonyls and hydrogen in strongly acidic solutions. We are therefore confronted with a situation which is not too different from that obtained by adding alkali metal modifiers, or for that matter, potassium or phosphorous adatoms to well-defined single crystals (8, 16). It is our thinking that an ensemble effect cannot be excluded.

In light of the vast experimental evidence which is suggestive of an electronic effect, we would be foolish to reject it outright. However, at this stage we feel that an electronic effect in the $CO-H_2$ reaction, unlike that in the ammonia synthesis, is secondary to a geometric effect brought about by site blocking of the Ru ensembles by adatoms. Both the methanation and the Fischer–Tropsch reactions are sensitive to metal dispersion. The rate of both reactions is depressed on small supported metal crystallites, suggesting the requirement of a relatively large number of adjacent active metal

surface sites (31). If the role of the alkali metal modifier is similar to that of a surface diluent, such as Pt, the results of this study suggest that the hydrogenation step appears to be more sensitive to the size of the ensemble and to the manner in which carbon is bound to the surface than to the dissociation of CO.

It would be useful to direct one final comment to the results of Dry et al. (5), who actually report an increase in the methanation activity for alkali-promoted iron catalysts. There are two factors which should be considered: (1) Dry et al. (5) did not measure Fe surface areas, and therefore, the effect of alkali metal promoters on the surface areas remains uncertain; and (2) the addition of small amounts of alkali to an alumina support results in the segregation of the alkali metal atoms to the support. This occurs as a result of the neutralization of the acid sites on the alumina support by the alkali metal precursor. For this reason, the distribution of alkali metal atoms between the support and the metal particles may be quite different from studies in which silica is used as a support.

CONCLUSIONS

The following conclusions emerge from the results of this study:

(1) When hydrocarbon product distributions are compared at constant CH_4 turnover frequencies, rather than at constant temperature, differences between promoted and unpromoted supported Ru catalysts are small. This suggests that the promoter inhibits the hydrogenation step.

(2) Temperature-programmed desorption studies show that carbon deposition formed by the Boudouard Reaction is not enhanced as a result of the addition of alkali metal modifiers. A small increase in the binding energy was observed for the promoted catalysts. The increase in carbon formation under reaction conditions is therefore due to a decrease in the rate of the hydrogenation step.

(3) *In situ* infrared studies suggest that in

the presence of a promoter, CO is preferentially adsorbed on "on top" Ru surface sites. However, multiple adsorption is substantially increased.

(4) Our results suggest that an ensemble effect is more important than an electronic effect in considering the inhibition of the methanation rate.

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