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Methanation and Fischer–Tropsch Studies on Potassium-Promoted Silica-Supported Ru Catalysts

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The role of potassium as a promoter in the methanation and Fischer–Tropsch reaction has been studied. When the potassium content of a series of silica-supported Ru catalysts was increased, turnover numbers for both methane and hydrocarbon formation decreased. Significant increases in the selectivity for higher hydrocarbon and olefin formation occurred as the potassium concentration was increased. The results of a temperature-programmed desorption study showed that the binding sites of CO on Ru were significantly changed due to the presence of the potassium. When the potassium concentration was increased, the high-temperature desorption maxima centered at 370°C increased relative to the low-temperature desorption maxima at 200°C. This result is interpreted in terms of the stronger C–Ru bond resulting from the presence of the potassium. The results of the temperature-programmed desorption study were verified using *in situ* infrared spectroscopy. As the potassium content of the Ru–SiO_2 catalysts was increased, additional CO infrared bands assigned to more strongly bound CO were observed. An *in situ* infrared temperature-programmed reaction study for the potassium-promoted catalyst showed that the more weakly bound CO desorbed without undergoing reaction to form methane.

INTRODUCTION

The addition of small amounts of potassium to supported group VIII metals has long been known to enhance the formation of long chain hydrocarbons in the Fischer–Tropsch synthesis (*1*). The mechanism of this promotional activity although well known is not fully understood. A major problem in the reproduction of data using potassium-promoted supported group VIII metals has arisen due to segregation of the potassium to the support (*2*). Because the role of potassium as a modifier is maximized when the group VIII metal and the K_2O are in intimate contact with each other, the method of catalyst preparation becomes an important factor. Two synthetic methods have generally been used in the preparation of these catalysts. The support can be impregnated with an appropriate salt of the group VIII metal. Following reduction, a potassium salt is then added. Alternatively, the procedure can be reversed. Recently, Vannice and McVicker (*3*) have prepared potassium-promoted supported group VIII metals from potassium–group VIII metal carbonyl complexes. K/Fe catalysts prepared using this method were found to be more selective in the production of C_2–C_5 hydrocarbons. However, no major changes in hydrocarbon selectivity were observed for K/Ru catalysts prepared by this route.

In this paper, we report on the results of a methanation of Fischer–Tropsch study on silica-supported potassium-promoted ruthenium catalysts prepared by the coimpregnation of a silica support with KNO_3 and $RuCl_3 \cdot 3H_2O$.

METHODS

Apparatus. The flow system which enables use of the reactor as either a pulse microreactor or a single-pass differential flow reactor has been described in detail elsewhere (*4*). The reactor was constructed

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from 12-mm Pyrex glass tubing and had a total volume of 20 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). This enabled the selection of any desired heating schedule.

In several experiments, an infrared cell also capable of operating either as a pulse microreactor or a single-pass differential reactor was used in place of the Pyrex microreactor. This substitution enabled use of the infrared cell-reactor as a spectroscopic probe while simultaneously obtaining kinetic data. Details regarding the design of this infrared cell have been described elsewhere (*5*). However, an important feature of the infrared cell-reactor was that reactant gases were forced through the sample disk with little or no leakage occurring around the edges of the sample.

Materials. The gases used in this study were subjected to the following purification treatment: CO (New England Oxygen research grade, 99.6% purity) was further purified by passing it through a molecular sieve. H_2 (New England Oxygen research grade, 99.95% purity) was passed through a Deoxo unit to convert O_2 impurities to H_2O, which was then removed by a molecular sieve maintained at 77 K by means of a liquid N_2 trap. O_2 (New England Oxygen research grade) was purified by passing it through a dry ice–acetone bath to remove traces of H_2O. He (New England Oxygen high purity, 99.995%) was passed through an oxygen trap (model OT-1, Separations Co.) backed by a molecular sieve maintained at 77 K by means of a liquid N_2 trap. Because TPD and TPR studies are extremely sensitive to trace amounts of O_2 and H_2O in the carrier gas stream, care was taken to exclude these contaminants from the catalyst sample. The oxygen concentration in the carrier gas at the sample was measured and found to be about 0.1 ppm. H_2O levels were much lower. For the measurement of reaction rates, it was found more convenient to use H_2 and CO (New England Oxygen research grade) premixed in a 3 : 1 ratio. This mixture was diluted with He to produce a reactant feed stream having the desired gas composition.

The silica-supported samples used in this study were prepared by impregnation or coimpregnation. Initially, the appropriate weight of $RuCl_3 \cdot 3H_2O$ (Strem Chemical) and KNO_3 (Mallinckrodt, analytical reagent grade) was dissolved in an amount of deionized water sufficient to ensure the complete wetting of the silica support. The solutions were mixed with Cab-O-Sil, Grade M-5 (Cabot Corp., Boston, Mass.) until a slurry having the consistency of a thin paste was formed. The slurry was dried in a vacuum desiccator at room temperature for 1 or 2 days and stirred regularly during the drying process to retain uniformity. The dried catalyst was then ground into a fine powder before use.

Procedure. A fresh catalyst was treated as follows: evacuated at 127°C for 1 hr, temperature increased in flowing H_2 from 127 to 327°C at about 10°C/min, reduced in flowing H_2 (25 ml/min) at 327°C for 2 hr, followed by evacuation at 447°C for 30 min. In the case of the unpromoted Ru samples about 200 mg of the catalyst was mixed with 100 mg of Cab-O-Sil. This served to dilute the catalyst bed thereby reducing catalyst temperature gradients. In the case of the potassium-rich catalysts, 300 mg of catalyst was used. Following the initial pretreatment, the catalyst was isolated from the pretreatment vacuum system by means of two four-way stopcocks and transferred to the reaction flow system. The potassium present on the catalyst surface following this pretreatment was K_2O.

The reactant mixture, which consisted of a H_2–CO feed stream having a premixed ratio of 3 : 1 diluted with He, was reacted over the catalyst at the desired reaction temperature until the reaction rate was stabilized (usually 30–60 min). Conversions ranged from 2% on the potassium-rich catalysts to 15% on the unpromoted Ru catalyst. Product analysis was performed using a Perkin-Elmer model 3-B gas chromatograph. Adequate hydrocarbon separation was obtained by means of a 3-m stainless-steel column, 3.175 mm in diameter, packed with chromosorb 106. The temperature was ramped between 50 and 200°C and the column was kept free of H_2O by means of a dry-ice trap placed in the line. Using this separation technique olefins and paraffins through C_5 were adequately resolved.

Adsorption measurements were made with the associated flow system set up to operate as a pulse microreactor. Measured volumes of CO or O_2 (100 μl) were pulsed through the catalyst until the height of successive eluted peaks observed on the gas chromatograph had identical heights. In these measurements a 0.15-m stainless-steel column, 3.175 mm in diameter, packed with carbosieve S and maintained at 50°C was used.

Temperature-programmed reaction and temperature-programmed desorption studies could be performed either in the Pyrex microreactor or directly in the infrared cell-reactor. Following the adsorption of the reactant gases, temperature-programmed desorption studies were carried out in flowing He by increasing the temperature linearly. When these studies were performed directly in the infrared cell, both the product distribution and the structure of the chemisorbed species remaining on the surface were monitored simultaneously by means of a gas chromatograph and an infrared spectrometer. Identical procedures were followed in the temperature-programmed reaction studies, except that the carrier gas was switched from He to H_2. All infrared measurements were obtained using a Perkin-Elmer model 281 infrared spectrophotometer interfaced with a Perkin-Elmer Data Station to facilitate data processing. The powdered catalyst was pressed into self-supporting discs for use in the infrared cell-reactor. The discs had a diameter of 25.4 mm and an optical density of about 0.2 mg mm^{-2}.

RESULTS AND DISCUSSION

Rate Measurements

Turnover numbers for C_1, C_2 and C_3 hydrocarbon formation at 220°C are shown in Fig. 1. These results show a sharp drop in the turnover number as the potassium concentration is increased. This decrease in reaction rate has been observed by others (*3*), and is not due to a loss in surface area with increasing potassium content. Metal dispersions as measured by both O_2 and CO chemisorption increased from 13% on unpromoted Ru to 19% on the 10% K/Ru catalyst. CO uptake on $K_2O–SiO_2$ samples was found to be negligible. A complete summary of the chemisorption and kinetic data is shown in Table 1. Activation energies for methane formation were observed to increase on the potassium-promoted Ru catalysts in good agreement with results reported by McVicker and Vannice (*3*). Turnover numbers for methane formation were observed to drop at a faster rate than those for C_2 and C_3 hydrocarbon formation as the potassium content was increased. An overall drop in the rate by a factor of 20 was observed for methane formation as compared to a factor of 5 for C_2 and C_3 hydrocarbon formation. From these results, it is

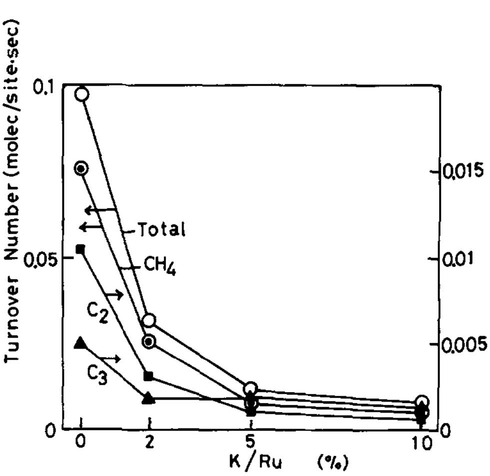


FIG. 1. Turnover numbers for hydrocarbon formation as a function of potassium content for promoted silica-supported Ru catalysts at 220°C.

TABLE 1

Summary of Kinetic Data for Methane Formation over Silica-Supported K-Promoted Ru Catalysts

Catalyst[a] Ru–K (K%)	Dispersion[b] (%)	Turnover number at 220°C (molec. site^{-1} sec^{-1} × 10^3)			E (kcal/mole)	Selectivity at 220°C		
		CH_4	C_2	C_3		To CH_4[c]	C_3/C_2	C_3^{2-}/C_3^-
0	12.5	75.8	10.6	7.10	25.0	77.3	0.66	0.13
2	16.8	26.3	2.9	1.82	29.3	82.2	0.63	0.16
5	18.6	7.37	1.27	1.97	31.1	63.5	1.49	1.62
10	19.1	3.97	0.79	1.29	30.6	57.1	1.54	13.2

[a] Metal loading; 3% Ru by weight.

[b] Measured by CO chemisorption at 25°C.

[c] CH_4 selectivity = $\sum_{n=1}^{n=5} \frac{C_1}{nC_n}$.

apparent that the term "potassium promoter" is somewhat of a misnomer when applied to this particular reacting system. Because all reaction rates are noticeably decreased by the addition of potassium, it is evident that it is acting as a selective poison rather than a promoter.

In Fig. 2, methane selectivities $\left(\text{defined as } \sum_{n=1}^{n=5} \frac{C_1}{nC_n}\right)$ are shown as a function of temperature. The addition of small concentrations of potassium had virtually no effect on methane selectivity. However, as potassium levels were increased to 5 and 10%, respectively, the methane selectivity was observed to drop from 95% (0% K) to 70% (10% K) at 240°C. The formation of hydrocarbons containing more than five carbon atoms was negligible under the conditions of the present study and were not taken into account in computing selectivities.

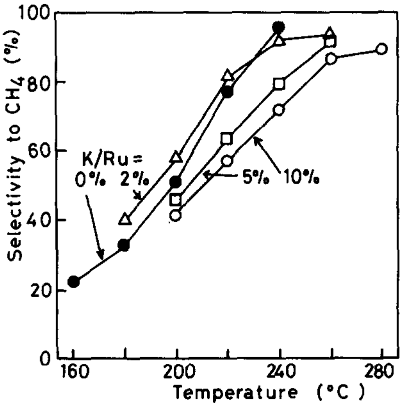


FIG. 2. Methane selectivity as a function of potassium content and temperature for promoted silica-supported Ru catalysts.

Figure 3 shows the dependence of the C_3/C_2 hydrocarbon ratio on potassium concentration. When the concentration of potassium was increased from 0 to 10%, the C_3/C_2 hydrocarbon ratio increased by about an order of magnitude at 240°C. The dependence of the olefin-paraffin ratio (C_3^{2-}/C_3^-) on potassium concentration, shown in Fig. 4, was even more dramatic. It increased by two orders of magnitude at 220°C as the potassium concentration was increased from 0 to 10%.

Because reaction rates on the potassium-promoted catalysts were considerably lower than on the unpromoted catalysts, percentage conversions at 220°C based on total CO converted ranged from 15% on the unpromoted catalyst to 2% on the 10% potassium catalyst. In view of these rather large differences in CO conversion levels, it was necessary to study the effect of percentage CO conversion on both the C_3/C_2

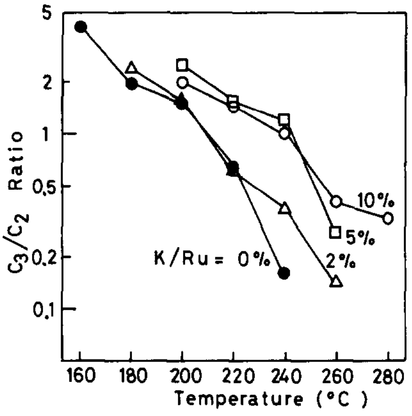


FIG. 3. C_3/C_2 hydrocarbon ratio as function of potassium content and temperature for promoted silica-supported Ru catalysts.

hydrocarbon ratio and the olefin–paraffin ratio. This study was performed by varying the space velocity at 220°C from 1500 to 5000 hr^{-1}. The results of this study on silica-supported Ru are shown in Fig. 5. With the exception of the olefin–paraffin ratio, it appears that the hydrocarbon distribution is rather insensitive to contact time and consequently on percentage CO conversion. The very large differences in the olefin–paraffin ratio observed cannot be accounted for solely on the basis of differences in the CO conversion. The olefin–paraffin ratio changed by a factor of 3 over the range of space velocities studied as compared to the two orders of magnitude observed when the potassium concentration was increased from 0 to 10% of the Ru metal loading. From these results it must be concluded that the addition of potassium to silica-supported Ru has a marked catalytic effect on the formation of olefins in the Fischer–Tropsch reaction. From these results, we conclude that the role of potassium as a modifier is to shift the rate of methane formation to higher temperatures. The rate of formation of Fischer–Tropsch products, on the other hand, appears to be less sensitive to variations in potassium loading. It is conceivable that these differences in reactivity could be due to a modification in the binding states of CO brought about by the presence of the potassium.

In order to clarify the role of potassium as a modifier in the preferential formation of olefins and higher hydrocarbons in the Fischer–Tropsch synthesis, a series of temperature-programmed desorption studies were performed on the potassium-promoted catalysts. In performing TPD studies on porous catalysts, care should be taken to consider the possibility of readsorption following desorption from a primary adsorption site. Recently, Herz *et al.* (*6*) have reviewed the variables which affect peak temperatures in TPD studies on porous catalysts. They concluded that irregardless of whether desorption occurs into a vacuum or into a carrier gas, adsorption–desorption equilibrium is maintained and, therefore, readsorption most certainly cannot be neglected. The net effect of readsorption is to widen the desorption maxima corresponding to a given adsorbed species and to shift the position of the desorption maxima to higher temperatures. Critical variables which affect the position of the desorption maxima include: (i) carrier gas flow rate, (ii) catalyst porosity, and (iii) total metal surface area. Because of these considerations,

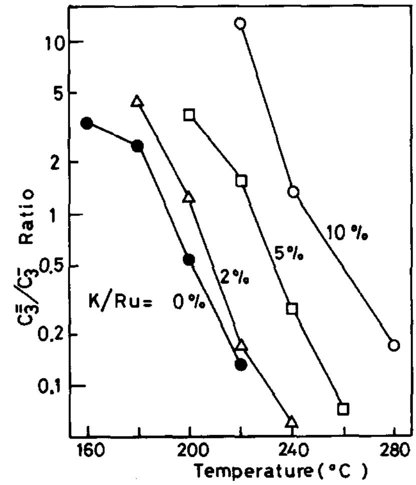


FIG. 4. Olefin to paraffin ratio for C_3 hydrocarbons as a function of potassium content and temperature for promoted silica-supported Ru catalysts.

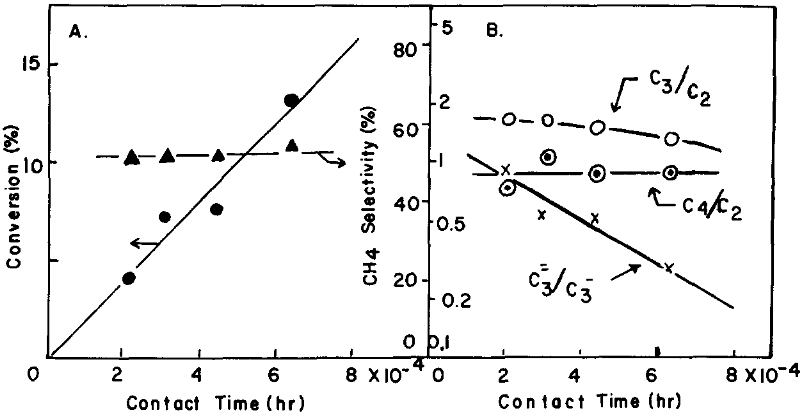


FIG. 5. The effect of contact time and percentage conversion on the hydrocarbon product distribution for an unpromoted silica-supported Ru catalyst at 220°C.

comparisons between TPD chromatograms from different catalyst samples are strictly valid only when these variables are held constant. These considerations do not preclude qualitative comparisons of TPD data from different catalysts provided that care is taken to ensure that the above variables are held constant. For this reason, therefore, we have kept both the carrier gas flow rate and metal catalyst surface area constant.

In these studies, both CO_2 and CO were monitored as a function of desorption temperature. The TPD spectra of CO on the unpromoted catalyst is shown in Fig. 6. The temperature corresponding to maximum CO desorption occurred at 200°C in good agreement with published data (*7*, *8*). A second CO desorption peak centered at about 370°C was poorly developed. This high-temperature peak was also observed by Low and Bell (*7*) on alumina-supported Ru and by Zagli and Falconer (*9*) on silica-supported Ru. In both these studies, the intensity of the high-temperature peak was much greater than that reported in this study. The relative intensities of the TPD bands corresponding to the desorption maxima have been the subject of some controversy. Nijs (*10*) has observed that the ratio of the relative intensities of the two bands could vary between 0 and 3 and was dependent on the metal dispersion. Recently, Lee *et al.* (*11*) studied the TPD of CO from single crystals of Ru(001). They concluded that the high-temperature desorption state depended on the presence of a certain but yet undetermined surface structure. The relative intensity of the high-temperature desorption maxima was also found to increase on the addition of small amounts of preadsorbed O_2 and H_2O. For this reason support effects in addition to the presence of small amounts of H_2O arising from the dehydroxylation of the support could be expected to influence the intensity of the high-temperature maxima. In order

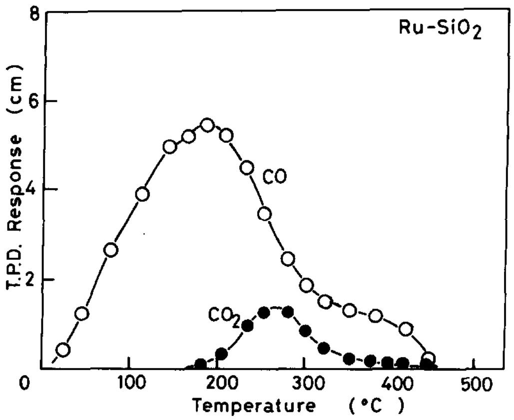


FIG. 6. Temperature-programmed desorption spectra of CO and CO_2 from unpromoted silica-supported Ru.

to minimize the effect of H_2O on the desorption of CO and also to depress CO_2 formation via the water–gas shift reaction, the catalyst was evacuated at 450°C prior to performing a TPD study. In the present study, the desorption maxima corresponding to CO_2 formation was observed as a single maxima centered at about 280°C. We attribute this CO_2 formation to the Boudouard reaction rather than the water–gas shift reaction. If CO_2 were formed as a result of the water–gas shift, CO_2 formation would remain high due to an increase in the rate at higher temperatures. The fact that CO_2 formation goes to zero under conditions in which CO is still desorbing from the catalyst argues against the water–gas shift reaction.

TPD spectra for the potassium-promoted catalysts are shown in Fig. 7. There was a marked difference in the binding states of CO as the concentration of potassium was increased. The main feature associated with this change was the increase in the intensity of the high-temperature CO desorption maxima. The addition of the potassium promoter apparently increased the number of Ru metal sites to which CO was strongly bound.

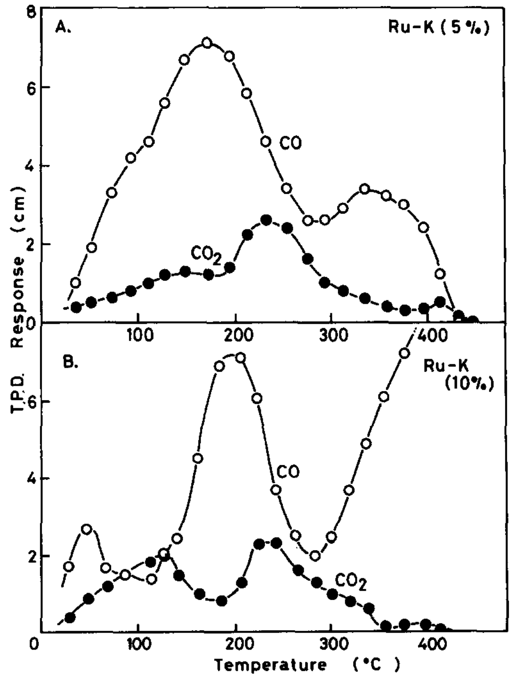


FIG. 7. Temperature-programmed desorption spectra of CO and CO_2 from potassium-promoted silica-supported Ru catalysts.

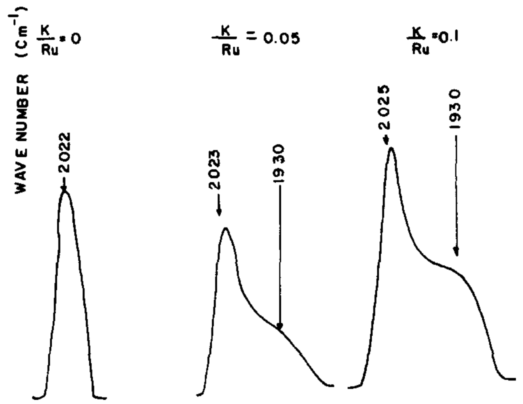


FIG. 8. Infrared spectra obtained under reaction conditions at 220°C: (A) unpromoted silica-supported Ru; (B) potassium-promoted silica-supported Ru, K/Ru = 0.05; (C) potassium-promoted silica-supported Ru, K/Ru = 0.1.

To obtain a better understanding of the binding states of CO present on the surface under reaction conditions, infrared spectra were obtained for both the promoted and unpromoted catalysts at process pressures and temperatures during the reaction. These spectra are shown in Fig. 8. Only one rather symmetric CO band centered at 2020 cm^{-1} was observed for the reaction on the unpromoted catalyst (Fig. 8A). This band has previously been assigned to the CO stretching vibration for CO linearly adsorbed on Ru (*12*). However, it was shifted from 2034 to 2020 cm^{-1} due to the presence of H_2. As the concentration of potassium was increased (Figs. 8B and C), a low-frequency shoulder centered at about 1930 cm^{-1} was observed. In addition to this band, a third infrared band centered at 1800 cm^{-1} was also observed. Both the 1930 cm^{-1} shoulder and the 1800 cm^{-1} band were observed to intensify with increasing potassium content. Unfortunately, the 1800 cm^{-1} band was not as well resolved as might be expected due to shifts in the baseline with increasing temperature. It is generally agreed that infrared bands assigned to the stretching mode of CO above 2000 cm^{-1} are due to CO adsorbed on centers of high surface coordination. Infrared bands centered at wave numbers below 2000 cm^{-1} are due to CO adsorbed on surface centers of low surface coordination (*13*). CO adsorbed on centers of low surface coordination is generally more tightly bound to the metal due to increased back donation from the d orbitals of the metal into the antibonding Π^* orbitals of the CO (*14*). The infrared data are, therefore, in excellent agreement with the TPD data. As the concentration of the potassium promoter is increased, the asymmetry of the CO band to the low-frequency side in addition to development of the 1930 cm^{-1} shoulder and the 1800 cm^{-1} band are consistent with an increase in the binding energy of CO to Ru surface sites.

An *in situ* TPD study in the infrared cell could not be performed due to experimental restrictions on the upper temperature limit imposed by the optical lenses used in the infrared cell (polycrystalline CaF_2). However, the relative reactivity of the various CO chemisorbed species was studied using an *in situ* temperature-programmed reaction technique. In this study, it was possible to measure both the rate of CO desorption and CH_4 formation while simultaneously measuring the absorbance of the CO bands due to adsorbed CO. The TPR was carried out in flowing H_2 as the temperature was linearly increased at a rate of 10°C/min. The result of this study for the 10% K/Ru catalyst is shown in Fig. 9. The data clearly show that the weakly bound CO is more unreactive than the CO which is adsorbed on sites of low surface coordination. A significantly large volume of CO was observed to desorb at low temperatures without undergoing reaction with H_2. This initial desorption of CO was paralleled by a much sharper decrease in the absorbance of the 2020–2000 cm^{-1} band than that of the 1950–1920 cm^{-1} shoulder. Methane formation was observed to occur at temperatures in excess of 150°C. At this temperature, the absorbance of both infrared bands was observed to decrease sharply. However, the absorbance of the 1950–1920 cm^{-1} band was not significantly reduced until methane formation was observed to occur. The reactivity of the CO species giving rise to the infrared band centered at 1800 cm^{-1} was difficult to determine. The absorption band was small and variations in the baseline with changes in temperature in this spectral region made it difficult to measure absorbances precisely. However, the reactivity of this species roughly paralleled that of the CO species responsible for the infrared band at 2020–2000 cm^{-1}.

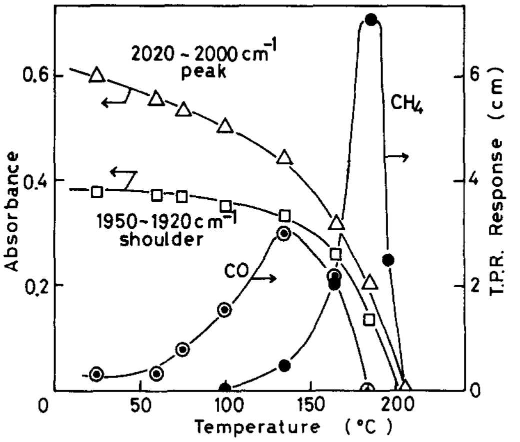
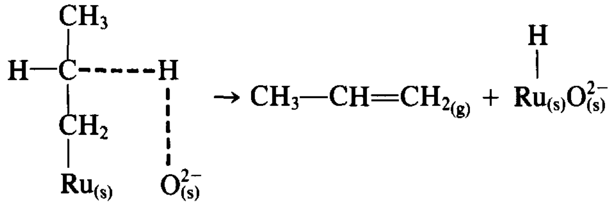


FIG. 9. Simultaneous infrared and temperature-programmed reaction study for the reaction $CO_{(s)} + H_{2(g)}$ from a potassium-promoted silica-supported Ru catalyst, K/Ru = 0.1.

There is a significant difference between the TPR spectra for the potassium-promoted Ru catalyst (Fig. 9) and that obtained for the unpromoted Ru catalyst (*15*). These differences are somewhat qualitative in nature because the CO was preadsorbed in He in the case of the unpromoted catalyst and in H_2 for the potassium-promoted catalyst. In the case of unpromoted Ru, only trace amounts of CO were observed to desorb prior to undergoing reaction to form methane. The temperature corresponding to the maximum rate of methane formation on the unpromoted Ru catalyst occurred at about 140°C as compared to 200°C for the 10% K catalyst. The effect of potassium as a catalytic modifier in the methanation reaction is then to increase the temperature corresponding to incipient methane formation thereby reducing the methanation rate. Because the Fischer–Tropsch reaction is inhibited to a lesser extent than the methanation reaction, it is apparent that the role of potassium as a catalytic modifier is to limit CH_4 formation in preference to hydrocarbon chain growth.

It would be speculative to suggest that only the more strongly bound CO in the case of the potassium-modified catalysts is the species which is undergoing reaction. For a gas with an adsorption probability near one, a molecule will strike the walls of a pore so often that adsorption and desorption will be near equilibrium. Therefore, observing reaction products from a given desorption state does not imply that that desorption state is reacting. It is clear, however, that a large fraction of the more weakly bound CO, is desorbed prior to undergoing reaction with H_2 to form methane.

It is reasonable to attribute the stronger binding states of CO on the potassium-promoted catalysts to the electron donation properties of K_2O. An increase in the electron density on Ru surface sites, which are in close proximity to the promoter molecules, would result in an increase in the strength of carbon–metal bond by virtue of the back donation of electron from the *d*-orbitals of the metal to the Π* antibonding molecular orbitals of CO. These potassium-promoted surface sites which bind carbon monoxide more strongly could also be responsible for an increase in the yield of olefins. The view is generally held that the growing hydrocarbon chains are oriented perpendicular to the metal surface (*16, 17*). On a Ru surface site promoted by K_2O we can envision the following mechanism to be operative:



$$\rightarrow CH_3{-}CH{=}CH_{2(g)} + Ru_{(s)}\overset{H}{O}{}^{2-}_{(s)}$$

In the absence of the K_2O promoter, the addition of a hydrogen atom to the growing hydrocarbon chain occurs at a faster rate than the abstraction of a β hydrogen atom from the adsorbed hydrocarbon thereby increasing the rate of paraffin formation.

CONCLUSIONS

The following important conclusions emerge from this study:

(1) Potassium-promoted silica-supported Ru catalysts prepared by coimpregnation selectively poison the methanation reaction. This results in an increase in the selectivity for Fischer–Tropsch products.

(2) The addition of potassium as a catalytic modifier, results in stronger CO adsorption on K_2O promoted surface sites.

(3) TPR studies show that on potassium-promoted Ru catalysts, CO reacts with H_2 to form methane at higher temperatures than on unpromoted Ru catalysts.

ACKNOWLEDGMENT

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