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The Preparation, Characterization, and Use of Supported Potassium–Group VIII Metal Complexes as Catalysts for CO Hydrogenation

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A major disadvantage of supported Group VIII metal Fischer–Tropsch catalysts, when compared to bulk catalysts, is the difficulty in effectively promoting such catalysts with potassium. A novel approach for preparing well-dispersed, highly promoted potassium–Group VIII metal catalysts has been developed. Catalysts were prepared by impregnating Al_2O_3 or SiO_2 with well-characterized potassium–Group VIII metal carbonyl complexes and then thermally decomposing the supported complexes under hydrogen. Since potassium and the Group VIII metals are associated in the precursor complexes, the deposition and subsequent decomposition of such complexes maximize potassium–Group VIII metal contacting on the support surface. Several complex derived catalysts were found to be more active and to exhibit higher selectivities for C_2–C_5 olefins than conventionally prepared potassium–Group VIII metal catalysts of the same metals stoichiometry. These results suggest that the use of preformed carbonyl complexes as supported catalyst precursors can increase any promotional effect potassium can have upon supported Group VIII metals.

INTRODUCTION

Potassium has long been known to enhance the formation of both longer chain and olefinic hydrocarbons from CO and H_2 over bulk iron catalysts, which are used in the Fischer–Tropsch synthesis reaction (*1*). Potassium, however, facilitates the sintering of metal crystallites and has been shown to reduce iron surface areas markedly (*2*). To minimize sintering, oxide supports such as SiO_2 and Al_2O_3 have been used to stabilize Group VIII metal surface areas (*3–5*). The use of high-surface-area supports tends, however, to reduce direct potassium–Group VIII metal contact since the metals typically cover only a small fraction of the support surface. Thus, in the preparation of Group VIII metal Fischer–Tropsch catalysts, a careful balance between promotional and stabilization additives must be achieved to maximize activity and selectivity patterns.

Bulk Group VIII metal catalysts are poorly dispersed and thus possess low surface/volume ratios. Supported Group VIII metal catalysts, however, have much smaller crystallite sizes and correspondingly higher metal surface/volume ratios. Supports also function to stabilize small Group VIII metal crystallites against thermal sintering (*5*). The major disadvantage of well-dispersed, supported Group VIII metal catalysts is the difficulty in effectively promoting such catalysts with potassium. The difficulty arises since the added potassium promoter has a tendency to preferentially affix itself to the high-surface-area support rather than to the small Group VIII metal crystallites (*6*). This reduces the promotional effect of potassium on the Group VIII metal component.

Typically, supported Fischer–Tropsch catalysts are prepared by first impregnating

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a carrier with a Group VIII metal salt. After reduction of the Group VIII metal salt, a potassium salt is then deposited and decomposed. Conversely, a support may be first impregnated with a potassium salt, then subsequently impregnated with a Group VIII metal salt, and finally reduced. In this study, conventional supported catalysts were prepared by the coimpregnation of potassium and Group VIII metal salts onto a carrier and then reducing under flowing hydrogen.

This paper is primarily concerned with describing a novel preparation of supported, potassium-promoted Group VIII metal catalysts and characterizing their catalytic behavior toward the CO hydrogenation reaction. The catalysts were prepared by impregnating a high-surface-area support with a soluble potassium–Group VIII metal carbonyl complex and then thermally decomposing the supported complex under hydrogen. The use of preformed potassium–Group VIII metal carbonyl complexes as precursors for the preparation of supported Fischer–Tropsch catalysts is a promising synthetic technique (*7*). First of all, the technique provides a route for preparing well-dispersed Group VIII metal phases. This aspect is particularly important with regard to iron catalysts, which are notoriously difficult to prepare in a highly dispersed state. Second, the stoichiometry of the potassium–Group VIII metal carbonyl complexes can be defined, thereby allowing control over the number and type of metal atoms in a given complex. Thus a wide range of supported K/metal stoichiometries is possible using such complexes as catalyst precursors. Third, the presence of Group IA metals, especially K and Rb, are well known to promote Group VIII metals for the Fischer–Tropsch synthesis reaction. Since potassium and the Group VIII metals are in intimate contact in the precursor complexes, the deposition and subsequent reductive decomposition of such complexes on a support surface should facilitate K–Group VIII metal contact and maximize the promotional effect of potassium.

The use of supported complex derived catalysts, prepared by the above-cited technique, in Fischer–Tropsch synthesis reactions will also be described. Several complex derived catalysts were found to exhibit beneficial changes in that they demonstrate an enhanced selectivity for the production of olefins and yield a markedly lower methane make than conventional unpromoted and potassium-promoted Group VIII metal Fischer–Tropsch catalysts.

EXPERIMENTAL

Preparation of Catalysts

Air-sensitive reactions and catalyst preparations using air-sensitive complexes were carried out in a "dry box" employing a nitrogen atmosphere. Solvents were dried and degassed by standard techniques (*8*). Preparative procedures for the different catalysts are as follows. All metal loadings are in weight percentages.

(*A*) *5.5% K, 3.9% Fe/*Al_2O_3. The precursor complex, $K_2Fe(CO)_4 \cdot 2C_4H_8O$, was prepared by reducing $Fe_3(CO)_{12}$ with potassium metal chips in dry THF solution (*9*). The solid off-white $K_2Fe(CO)_4 \cdot 2C_4H_8O$ complex was collected by vacuum filtration, washed with *n*-heptane, and vacuum (1.3×10^{-2} Pa) dried. $K_2Fe(CO)_4 \cdot 2C_4H_8O$, 1.51 g, was dissolved in 6.0 ml of dry methanol. The resulting dark-yellow solution was used to impregnate 9.8 g of dry η-Al_2O_3 (dried at 623 K, 4.0 hr at 1.3×10^{-2} Pa). The alcohol solvent was removed by evacuation at room temperature. A second impregnation was carried out using a solution containing approximately 0.75 g of $K_2Fe(CO)_4 \cdot 2C_4H_8O$ dissolved in 5.0 ml of methanol. The alcohol solvent was again removed by evacuation (1.3×10^{-2} Pa) at room temperature. The unreduced catalyst is extremely air sensitive and undergoes a rapid exothermic decomposition when exposed to oxygen. The vacuum-dried catalyst was decomposed at 773 K for 2.0 hr under a mixture of 20% H_2 in He flowing at 500 cm^3/min. The reduced catalyst was found to contain 5.5% K, 3.9% Fe (K/Fe = 2.0) (*10*).

(*B*) *2.2% K, 3.2% Fe/*Al_2O_3. The precursor complex, $KFe(CO)_2(C_5H_5)$, was prepared by reducing a 100-ml THF solution containing 3.17 g of $[Fe(CO)_2(C_5H_5)]_2$ with 1.0 g of potassium metal chips (*11*). The crude reaction mixture was filtered, and the clear-yellow filtrate was adjusted to 100 ml by addition of THF. Fifteen milliliters of this stock solution was used to impregnate 20 g of dry η-Al_2O_3 (dried at 623 K, 4.0 hr, 1.3×10^{-2} Pa). The solvent was removed by evacuation at room temperature. This impregnation–vacuum drying sequence was repeated seven times. The unreduced catalyst is extremely air sensitive and undergoes a rapid exothermic decomposition when exposed to oxygen. The vacuum-dried catalyst was decomposed at 773 K for 2.0 hr under 20% H_2 in He flowing at 500 cm^3/min. The reduced catalyst was found to contain 2.2% K, 3.2% Fe (K/Fe = 1.0) (*10*).

(*C*) *6.7% K, 4.7% Fe/*SiO_2. $K_2Fe(CO)_4 \cdot 2C_4H_8O$, 1.51 g, was dissolved in 11.0 ml of dry methanol. The resulting dark-yellow solution was used to impregnate 5.0 g of SiO_2 which was previously dried for 16 hr at 823 K under flowing dry air. The solvent was removed by evacuation at room temperature. The unreduced catalyst is extremely air sensitive and undergoes a rapid exothermic decomposition when exposed to oxygen. The vacuum-dried catalyst was decomposed at 773 K for 2.0 hr under 20% H_2 in He flowing at 500 cm^3/min. The reduced catalyst was found to contain 6.7% K, 4.7% Fe (K/Fe = 2.0) (*10*).

(*D*) *0.45% K, 1.3% Ru/*Al_2O_3. The precursor complex, $K_2Ru_3(CO)_{12}$, was prepared by reducing 0.843 g of $Ru_3(CO)_{12}$ with 30 g of a 1% K amalgam in 30 ml of dry THF under 445 kPa CO pressure. Reduction of triangular $Ru_3(CO)_{12}$ occurs via the cleavage of a single Ru–Ru bond producing thereby a linear dianion (*12*). The crude reaction mixture was filtered, and the dark-red filtrate was concentrated to 16 ml by evacuation at room temperature. The concentrate was used to impregnate 20 g of dry η-Al_2O_3 (dried at 743 K under flowing dry air for 72 hr). The THF solvent was removed by evacuation at 1.3×10^{-2} Pa at room temperature for 3.0 hr. The unreduced catalyst is extremely air sensitive. Following reduction the catalyst was found to contain 1.3% Ru, 0.45% K (K/Ru = 0.9) (*10*).

(*E*) *0.3% K, 1.4% Ir/*Al_2O_3. The precursor complex, $KIr(CO)_4$, was prepared by allowing 0.575 g of $Ir_4(CO)_{12}$ to react with 30 g of a 1% K amalgam in 30 ml of THF under 445 kPa CO pressure (*12*). The crude reaction mixture was filtered, and the cherry-red filtrate was concentrated to 15 ml by evacuation. The concentrate was used to impregnate 20 g of dry η-Al_2O_3 (dried at 743 K for 72 hr under flowing dry air). The solvent was removed by evacuation at 1.3×10^{-2} Pa at room temperature for 3.0 hr. The unreduced catalyst is extremely air sensitive. Following reduction the catalyst was found to contain 1.4% Ir, 0.3% K (K/Ir = 1.0) (*10*).

(*F*) *5.5% K, 3.9% Fe/*Al_2O_3 *(conventional catalyst)*. A 6.0-ml solution containing 2.8 g $Fe(NO)_3)_3 \cdot 9H_2O$ and 1.4 g KNO_3 dissolved in distilled water was used to impregnate 9.1 g of dry η-Al_2O_3 (dried at 403 K for 16 hr under air). The impregnate was dried at 393–403 K for 72 hr under dry air. The dry catalyst was reduced under H_2 and contained 3.9% Fe, 5.5% K (K/Fe = 2.0) (*10*).

(*G*) *10% Fe/*Al_2O_3 *and 15% Fe/*Al_2O_3. The above conventional Fe/Al_2O_3 catalysts were prepared by heating solid $Fe(NO_3)_3 \cdot 9H_2O$ with η-Al_2O_3. The techniques of this procedure have been described elsewhere (*13*).

(*H*) *Bulk Fe*. The unsupported Fe catalyst used in this study was a red anhydrous ferric oxide obtained from the Fischer Chemical Company.

(*I*) *Bulk K/Fe*. The unsupported K/Fe

(1/100 mole ratio) catalyst used in this study was prepared by soaking Fe_2O_3 in an aqueous K_2CO_3 solution and then drying at 393 K for 16 hr.

Equipment and Procedures

(*A*) *Chemisorption measurements.* Carbon monoxide chemisorption studies were performed with a conventional glass high-vacuum system (*14, 15*). Samples weighing 1 to 4 g and sieved to size 20–40 mesh were placed in flow-through Vycor cells. Samples were reduced at 723 K under hydrogen (100 cm^3/min) for 1.0 hr. The reduced samples were cooled to 673 K under hydrogen and evacuated at this temperature for 1.0 hr. The sample was then cooled under dynamic vacuum ($<10^{-3}$ Pa) to room temperature. Carbon monoxide uptakes were determined at 298 ± 2 K. Typically, 30–60 min were allowed for each uptake point. The CO/metal ratios were calculated by determining the CO isotherm on the reduced, evacuated samples and assuming that this represented the sum of CO weakly bound to the support and strongly bound to the metal. The sample was then evacuated 10 min at room temperature and a second CO isotherm was measured. Since the second isotherm measures only the CO weakly bound to the support, the difference between the two isotherms gives the amount of CO irreversibly adsorbed on the metal. In accordance with previous studies, the amount of strongly bound CO at 133 Pa (100 Torr) was chosen as saturation coverage of the metal (*16*).

(*B*) *X-Ray diffraction measurements.* A Philips Electronics X-ray diffractometer (XRG-3000) with nickel-filtered Cu$K\alpha$ radiation was used for X-ray diffraction studies. Metal and metal oxide crystallite sizes were calculated from line broadening data, following procedures described elsewhere (*17*).

(*C*) *Infrared measurements.* Prior to decomposition under hydrogen, vacuum-dried, supported potassium–Group VIII metal carbonyl complexes were subjected to infrared measurements. Spectra in the carbonyl region were recorded on a Perkin-Elmer 621 spectrophotometer employing Nujol mull samples sandwiched between KBr salt plates. Samples were prepared in the strict absence of air and moisture.

(*D*) *Catalytic measurements.* Kinetic Fischer–Tropsch synthesis studies were carried out at 101 kPa (1 atm) in a glass reactor system employing 0.2–0.5 g of catalyst and utilizing a synthesis gas feed with a H_2/CO ratio of 3. Space velocities varied between 2400 and 4000 hr^{-1}. A Hewlett-Packard 7620 gas chromatograph employing Chromosorb 102 columns and subambient temperature programming was used for product analyses. Low conversions (usually 5% or less) were maintained to assure operation of a differential reactor and thereby eliminate effects due to heat and mass transfer, product inhibition, and secondary reactions. Catalysts were subjected to a standard pretreatment which consisted of a 0.5-hr reduction at 393 K, heating to 533 K and reducing for 0.5 hr, followed by heating to 723 K where the sample was further reduced for 1.0 hr. Hydrogen flowing at 30–50 cm^3/min was employed as the reducing agent. Catalysts were then cooled to the desired reaction temperature under hydrogen. After 20 min on stream at the desired reaction conditions, a sample was taken for gc analysis. The catalyst was then cleaned in flowing hydrogen for 20 min while conditions were adjusted for the next run. This cycling technique is similar to that described by Sinfelt (*18*) and is quite successful in preventing deactivation. The gases used and the additional purification steps employed have been described previously (*15*).

RESULTS AND DISCUSSION

Infrared Studies

Freshly impregnated, vacuum-dried potassium–Group VIII metal carbonyl complexes supported on Al_2O_3 were studied by infrared spectroscopy (see Table 1). The

TABLE 1

Infrared Bands (cm^{-1}) in the Carbonyl Stretching Region of Al_2O_3-Supported Potassium–Group VIII Metal Carbonyl Complexes[a]

Catalyst	% K	% M	Precursor	Mull[b]	Precursor in solution
(A)	5.5	3.9	$K_2Fe(CO)_4$	1921sh 1877vs 1848sh 1746m-s	1920sh[c] 1883vs 1868sh
(B)	2.2	3.2	$KFe(CO)_2C_5H_5$	1842vs 1753vs	1846vs[d] 1768vs
(C)[e]	6.7	4.7	$K_2Fe(CO)_4$	1922sh 1867vs 1837sh 1750m	1920sh[c] 1883vs 1868sh
(D)	0.45	1.3	$K_2Ru_3(CO)_{12}$	2029sh 1997vs 1954sh	2033w[d] 1960sh 1946vs 1918sh 1891sh
(E)	0.3	1.4	$KIr(CO)_4$	1915vs 1881vs	1896vs[d] 1863sh

[a] Vacuum-dried, nonreduced catalysts.

[b] Nujol mull spectra of supported complex derived catalysts.

[c] Methanol solution.

[d] THF solution.

[e] SiO_2 support.

major results of such measurements are illustrated by the following examples. The mull infrared spectrum of a dry, nonreduced sample of catalyst B (2.2% K, 3.2% Fe/Al_2O_3) exhibited a pair of strong carbonyl bands at 1842 and 1753 cm^{-1}. The positions of these bands are close to those displayed by the $KFe(CO)_2C_5H_5$ precursor in THF solution (1864 and 1768 cm^{-1}) (*19*). These observations indicate that the $KFe(CO)_2C_5H_5$ complex remains intact on the partially dehydrated Al_2O_3 surface. In the absence of air no decomposition of the supported complex was detected over a period of several months. Upon air exposure, however, the supported $KFe(CO)_2C_5H_5$ complex rapidly decomposed as noted by the loss in intensity of the 1842- and 1753-cm^{-1} bands. During the initial stages of oxidation, bands due to $(Fe(CO)_2C_5H_5)_2$ (1991, 1952, and 1758 cm^{-1}) were present (*20*), but with time these also decreased in intensity. When subjected to hydrogen reduction, the organic portion of the complex is destroyed leaving behind potassium (or potassium oxide) and reduced iron phases which are presumably in close proximity on the alumina surface.

A mull spectrum of a dry, nonreduced sample of catalyst E (0.3% K, 1.4% Ir/Al_2O_3) exhibited a pair of strong carbonyl bands centered near 1915 and 1881 cm^{-1}. The positions of these bands are similar to those exhibited by the precursor $KIr(CO)_4$ complex in THF solution (1896 and 1863 cm^{-1}) (*21*). Thus, the $KIr(CO)_4$ precursor complex appears to remain intact on the dry Al_2O_3 surface. Upon exposure to air the 1915- and 1881-cm^{-1} carbonyl bands of the supported complex were rapidly lost. During the early stages of oxidation, new bands at 2062, 2030, 1972, and 1623 cm^{-1} formed at the expense of the 1915- and 1881-cm^{-1} bands. The three high-wavenumber bands are likely due to $Ir_4(CO)_{12}$ which formed during the oxidative decomposition of $KIr(CO)_4$ (*22*). The low-wavenumber band has been assigned to a surface iridium carbonate (*23*). Upon hydrogen reduction of the intact $KIr(CO)_4$ complex, the carbon monoxide ligands are removed leaving behind potassium (or potassium oxide) and reduced iridium metal surface species. The additional supported complex derived catalysts listed in Table 1 were found to behave similarly.

The above infrared measurements have indicated that potassium–Group VIII metal carbonyl complexes are relatively stable on partially dehydrated Al_2O_3 surfaces in the absence of oxygen; however, upon exposure to air the complexes are readily decomposed. The oxidation process is presumed to be irreversible. When subjected to hydrogen reduction, reduced Group VIII metal species are produced on the surface since chemisorption of CO occurs and IR bands from the organic portion of the precursor complexes are no longer present. The oxidation state of the potassium component is not known but is most likely +1. This novel method of catalyst preparation offers several potential advantages. Potassium promotion by the above procedure may be more favorable than by the coimpregnation of aqueous potassium and Group VIII metal salt solutions. In the latter case, good contacting between the Group IA and Group VIII metals requires that both metal salts be adsorbed at equivalent rates onto the Al_2O_3 surface. This situation is known not to be generally obeyed (*24*). The electrostatic interactions present in the precursor potassium–Group VIII metal carbonyl complexes would be expected, however, to maintain the heteroatoms in close proximity as the complex is decomposed (reduced) on the Al_2O_3 surface. In essence, a supported potassium–Group VIII metal carbonyl complex may reduce as a single entity, whereas deposited monomeric potassium and Group VIII metal salts possess vastly different reduction characteristics and, in fact, may not be in intimate contact on the support surface. The latter situation could result in separate, noncontacting phases of potassium and Group VIII metals which would minimize, if not eliminate, any promotional effect caused by potassium. The decomposition of potassium–Group VIII metal carbonyl complexes may also yield unique crystallite geometries on the support surface. The possibility exists that the reductive decomposition of a three-dimensional complex may yield uniform clusters within which the basic metal geometry of the starting complex is retained. At the very least, the use of comlex precursors should maximize K–Group VIII metal contacting on the surface of inorganic supports.

Chemisorption Studies

Uptakes of carbon monoxide on fresh and used catalyst samples are shown in Table 2. Carbon monoxide uptake on K/Al_2O_3 samples was negligible, and it was assumed that K does not interfere with the determination of the Group VIII metal surface areas. A fresh 5.5% K, 3.9% Fe/Al_2O_3 complex derived catalyst (catalyst A) was found to adsorb 105 μmole of CO/g catalyst. This uptake corresponds to a CO/Fe ratio of 0.15. Earlier studies by Garten have shown that a fraction of iron on Al_2O_3 is not reducible in hydrogen even at temperatures as high as 973 K (*25*). This behavior has been attributed to a strong interaction between iron and certain Al_2O_3 surface sites. The concentration of such sites has been estimated to be about 300 μmole g^{-1}, which corresponds to the number of acid sites on Al_2O_3 (*26*). It is possible, then, to render up to 300 μmole Fe g^{-1} inert toward chemisorption. If this quantity of irreducible iron is subtracted from the total iron loading of 700 μmole g^{-1}, the ratio of CO to reducible iron is raised to 0.26 for catalyst A. This value suggests that a substantial portion of the iron may be well dispersed. X-Ray diffraction measurements on a reduced sample of catalyst A showed an iron (100%) line on the shoulder of an Al_2O_3 line. An estimate of the iron crystallite size indicates the presence of 40–50 Å particles although the fraction of iron represented by this line is not known. It is perhaps coincidental that the particle size indicated by X ray corresponds to a dispersion of about 25%, which is in excellent agreement with the ratio of CO to reducible iron.

TABLE 2

Carbon Monoxide Adsorption on Supported Potassium–Group VIII Metal Complex Derived Catalysts

Catalyst[a]	CO uptake[b] (μmole/g)		CO/M[c]	
	Fresh	Used[d]	Fresh	Used[d]
(A) 5.5% K, 3.9% Fe/Al_2O_3	105	44.0	0.15	0.063
(B) 2.2% K, 3.2% Fe/Al_2O_3	—	14.0	—	0.024
(C) 6.7% K, 4.7% Fe/SiO_2	23.2[e]	—	0.028	—
(D) 0.45% K, 1.3% Ru/Al_2O_3	127	66.3	0.99	0.51
(E) 0.3% K, 1.4% Ir/Al_2O_3	47	43.0	0.65	0.59
(F) 5.5% K, 3.9% Fe/Al_2O_3 (conventional catalyst)	52.4	25.8	0.075	0.037

[a] Catalysts were reduced under H_2 at 723 K for 1.0 hr prior to CO adsorption measurements. Samples were not exposed to O_2 before reduction.

[b] Uptakes measured at 298 + 2K.

[c] *M* is the Group VIII metal concentration.

[d] Catalysts recovered from Fischer–Tropsch experiments.

[e] Reduced for a total of 4 hr at 723 K.

A fresh, reduced, conventionally prepared 5.5% K, 3.9% Fe/Al_2O_3 catalyst (catalyst F) was found to exhibit a CO/Fe ratio of 0.075. This value is half that shown by the comparably loaded complex derived catalyst (catalyst A). These results indicate that the use of a preformed $K_2Fe(CO)_4$ complex yields either a more highly dispersed or a more completely reducible (or both) iron phase than a conventional preparation.

A sample of catalyst A recovered after use in a Fischer–Tropsch experiment gave a CO/Fe value of 0.063. A conventionally prepared catalyst (catalyst F) subjected to the same Fischer–Tropsch conditions demonstrated a CO/Fe ratio of 0.037. Although both ratios are low, these results indicate that a supported K/Fe complex derived catalyst has the ability to retain a higher iron surface area than a conventionally prepared catalyst.

Carbon monoxide uptakes on potassium–iron complex derived catalysts were generally found to be higher on Al_2O_3 than on SiO_2 supports (compare catalysts A and C). A reduced example of catalyst C showed an Fe (100%) X-ray line indicating an average particle size of about 140 Å, which corresponds to a dispersion of around 8%. Taken together, the chemisorption and X-ray results suggest that iron is less well dispersed on SiO_2 than on Al_2O_3. This finding is in agreement with the observations of Garten and Vannice (*27*).

Fresh and used samples of supported K/Ru and K/Ir complex derived catalysts (catalysts D and E) were found to exhibit high carbon monoxide uptakes. The relatively high CO/M values suggest that Ru and Ir are initially well dispersed and remain so under the Fischer–Tropsh reaction conditions used in this study. X-Ray diffraction patterns of these catalysts were devoid of Group VIII metal lines which also indicates that the catalysts are fairly well dispersed.

Kinetic Studies

The detailed product analyses and activities for CO conversion of several bulk and supported iron catalysts are presented in Table 3. The most important aspects here are the low methane make and high olefin content of the C_{2+} hydrocarbons produced over the Al_2O_3-supported complex derived catalyst (catalyst A). The activity of this catalyst is 50 times higher on a gram Fe basis than a conventional K/Fe catalyst (catalyst F). At the low conversions attained with the latter catalyst, only methane and ethylene were detected as products whereas catalyst A produced over 60 wt% C_2–C_4 olefins. A conventional, nonpromoted 10% Fe/Al_2O_3 (catalyst G) exhibited similar activity, but produced much more

TABLE 3

Comparison of the Fischer–Tropsch Catalytic Behavior of Bulk and Supported Iron Catalysts[a]

Catalyst	T (°C)	CO Conv. (%)	Product distribution (wt%)									Activity (μmole CO min^{-1} g^{-1} Fe)
			C_1	$C_2^=$	C_2	$C_3^=$	C_3	$C_4^=$	C_4	C_5	C_{5+}^{+}	
(A) 5.5% K, 3.9% Fe/Al_2O_3	264	2.3	9	15	1	19	Tr	16	4	20	16	150
(complex derived catalyst)	271	3.5	10	14	2	26	Tr	20	4	13	11	227
(F) 5.5% K, 3.9% Fe/Al_2O_3 (conventional catalyst)	268	0.07	44	56	0	0	0	0	0	0	0	4.5
(G) 10% Fe/Al_2O_3 (conventional catalyst)	264	3.5	50	2	23	1	10	Tr	10	4	0	204
(H) Bulk Fe metal	264	4.9	24	5	31	7	8	Tr	16	7	2	12
(I) Bulk K/Fe	269	1.5	13	22	2	22	Tr	24		12	5	13

[a] $H_2/CO = 3.0$, 101 kPa (1.0 atm) total pressure.

methane and far fewer olefins that catalyst A. Reduced, unpromoted iron (catalyst H) produced primarily paraffins, while the addition of K_2CO_3 to the bulk iron (catalyst I) showed the expected effect of an alkali metal promoter-increased olefin formation. Activities on a gram Fe basis are naturally low for these last two unsupported iron catalysts. In contrast to the conventional catalysts, the K/Fe complex derived catalyst demonstrated both high activity and high selectivity to olefins.

The above comparisons indicate that the use of a preformed $K_2Fe(CO)_4$ complex increases the promotional effect potassium has upon supported iron. The complex derived catalyst (catalyst A) was found to be 40–50 times more active than a conventionally prepared catalyst (catalyst F) of the same metal loading. This difference cannot be explained by considering the twofold higher Fe dispersion displayed by catalyst A. The activity advantage demonstrated by catalyst A must reflect either better K–Fe contacting or subtle microstructural differences which result from the deposition of $K_2Fe(CO)_4$.

The Fischer–Tropsch product distribution and activity (CO conversion) patterns of several supported complex derived catalysts are summarized in Table 4. A comparison of catalysts A and B indicates that as the K/Fe mole ratio of the precursor complex decreases from 2/1 to 1/1, catalyst activity increased while the quantity of olefinic and higher molecular weight products is lowered. This trend is in good agreement with the well-known effect potassium concentration has on the Fischer–Tropsch product distributions of unsupported iron catalysts (*1*, *28*). A comparison of catalysts A and C, in which the same precursor complex, $K_2Fe(CO)_4$, was used, shows that a marked decrease in activity occurs upon changing from Al_2O_3 to a SiO_2 support. The support effect is consistent with the poor reducibility of iron on SiO_2. The presence of potassium in the Ru and Ir complex derived catalysts (catalysts D and E, respectively) does not influence product distributions in a significant manner. The activity of the Ru catalyst was found to be considerably higher than that of the Ir catalyst. Ruthenium is normally found to be a more active CO hydrogenation catalyst than iridium (*15*, *29*). The Ru and Ir complex derived catalysts display product distributions similar to unpromoted, Al_2O_3-supported catalysts although a somewhat lower methane make appears to occur over catalyst D (*15*). The lack of a significant promoting effect by potassium on unsupported metals other than iron has been observed in other studies (*30*).

The kinetic parameters measured in the CO hydrogenation reaction provide, perhaps, the strongest evidence that the potassium in these complex derived catalysts is altering the catalytic behavior of the Group VIII metal. Table 5 shows specific activities

TABLE 4

Fischer–Tropsch Product Distribution for Supported Complex Derived Catalysts[a]

Catalyst[b]	*T* (°C)	Product distribution (wt%)									Activity (% CO conversion)
		C_1	$C_2^=$	C_2	$C_3^=$	C_3	$C_4^=$	C_4	C_5	C_{6+}	
(A) 5.5% K, 3.9% Fe/Al_2O_3	264	9	15	1	19	Tr	16	4	20	16	2.3
(B) 2.2% K, 3.2% Fe/Al_2O_3	263	27	4	9	24		18		14	4	7.1
(C) 6.7% K, 4.7% Fe/SiO_2	279	60	24	0	16		0	0	0	0	0.18
(D) 0.45% K, 1.3% Ru/Al_2O_3	244	32	1	11	10	4	4	10	17	11	10.1
(E) 0.3% K, 1.4% Ir/Al_2O_3	285	72	15	13	0	0	0	0	0	0	0.51

[a] $H_2/CO = 3.0$, 101 kPa (1.0 atm) total pressure, 0.45 g catalyst.

[b] Catalysts prepared by the deposition of preformed carbonyl complexes.

TABLE 5

Kinetic Parameters of Potassium–Group VIII Metal Complex Derived Catalysts

$T = 275°C$, $P = 101$ kPa, $H_2/CO = 3$

Catalyst	N_{CH_4} ($sec^{-1} \times 10^3$)	N_{CO} ($sec^{-1} \times 10^3$)	E_{CH_4} (kcal/mole)	E_{CO} (kcal/mole)
(A) 5.5% K, 3.9% Fe/Al_2O_3	1.5	14	26.3 ± 0.5	36.5 ± 1.2
(B) 2.2% K, 3.2% Fe/Al_2O_3	22	104	26.6 ± 2.0	29.0 ± 3.3
15% Fe/Al_2O_3[a]	57	150	21.3 ± 0.9	25.9 ± 1.6
(C) 6.7% K, 4.7% Fe/SiO_2	0.7[b]	1.2[b]	1.8 ± 1.4	4.4 ± 1.9
(D) 0.45% K, 1.3% Ru/Al_2O_3	28	73	33.6	31.1
5% Ru/Al_2O_3[a]	181	325	24.2 ± 1.2	18.3 ± 1.0
(E) 0.3% K, 1.4% Ir/Al_2O_3	0.44	0.68	25.3	28.3
2% Ir/Al_2O_3[a]	1.8	2.6	16.9 ± 1.7	11.7 ± 3.2
(F) 5.5% K, 3.9% Fe/Al_2O_3 (conventional catalyst)	0.12	0.25	17	15

[a] From Ref. (*15*).

[b] Based on $CO_{(ads)}$ for fresh sample

for methane formation, N_{CH_4}, and CO conversion, N_{CO}, represented as turnover frequencies (molecules sec^{-1} $site^{-1}$). These values are based on metal surface areas determined by CO adsorption on used catalyst samples. All the complex derived catalysts demonstrated lower turnover frequencies than their unpromoted, alumina-supported counterparts (*15*). In addition, the potassium-promoted catalysts were found to demonstrate considerably lower methane formation selectivities (N_{CH_4}/N_{CO}) than their unpromoted counterparts. The presence of potassium in the Al_2O_3-supported complex derived catalysts also seems to markedly increase the activation energies for both methane formation and CO conversion. These trends may indicate a change in the reaction pathway over the potassium-promoted metal surfaces (*5*). The catalytic behavior of a SiO_2-supported complex derived catalyst is clearly different than that of an Al_2O_3-based catalyst (compare A and C). Further studies are required to understand these apparent support differences.

SUMMARY

Supported, potassium-promoted Group VIII metal catalysts have been prepared by the deposition and subsequent decomposition of preformed, well-characterized potassium–Group VIII metal carbonyl complexes on high-surface-area carriers (SiO_2 and Al_2O_3). Since potassium–Group VIII metal carbonyl complexes can be synthesized with varying K/metal ratios, a wide range of catalyst compositions is possible. This novel preparative technique yields well-dispersed K/Group VIII metal particles which may retain the stoichiometry and geometry of the precursor complex.

Several K/Fe complex derived catalysts were found to be more active and more selective for the production of C_2–C_5 olefins than conventionally prepared, supported, potassium-promoted iron Fischer–Tropsch catalysts. No major change in selectivity was observed for potassium-promoted Ru and Ir catalysts. Potassium–Group VIII metal complex derived catalysts typically showed significantly higher activation energies for CO hydrogenation compared to unpromoted, alumina-supported metals. These results suggest that the use of preformed complexes as catalyst precursors can increase any promotional effect potassium can have upon supported Group VIII metals. Additional characterization and Fischer–Tropsch activity studies of sup-

ported, potassium-promoted Group VIII metal complex derived catalysts are in progress.

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