JOURNAL OF CATALYSIS **105**, 359–365 (1987)

Selective Fischer–Tropsch Synthesis on Metal Powder Catalysts Prepared by the Potassium Reduction of Halides in THF

M. MIYAKE, K. TAKEBE, AND M. NOMURA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1, Yamada-oka, Suita, Osaka 565, Japan

Received August 12, 1986; revised December 16, 1986

Metal powders such as Fe, Co, Ni, Fe–Co, and Fe–Ni prepared by reducing metal iodides or bromides with potassium metal in refluxing THF were used as catalysts for Fischer–Tropsch syntheses. These metal powders contained very small particles and have large BET surface areas (28–36 m^2/g). The metal powder catalysts, such as Fe and Fe–Co (80 : 20), gave 1-butene with more than 35 wt% selectivity at a rather high CO conversion of over 10 wt% at 533–553 K, while products on the Co catalyst obeyed conventional Schulz–Flory type distribution. The Ni catalyst showed little activity. Effects of reaction variables (temperature, H_2/CO feed gas ratio, and composition of Fe–Co) were investigated.

INTRODUCTION

Many research works in Fischer–Tropsch (F–T) syntheses have focused on the development of catalysts which primarily produce economically valuable products, such as low-molecular-mass olefins. One extensively used method is the encapsulation of an active metal species into support cages such as zeolite. For example, Gates *et al.* reported that a Co/A zeolite catalyst, prepared by Cd vapor reduction of Co^{2+}, quantitatively produced propylene at 424 K and 6 atm at a relatively low steady-state conversion of about 1% (*1*).

On the other hand, metals prepared by the condensation of metal vapors in organic solvents have recently been reported to have excellent catalytic properties. Ozin and co-workers reported that Fe and Co/NaY zeolite prepared by the mild decomposition of bis(toluene)metal(0) complexes, which were generated by a rotary metal-vapor solution-phase synthetic technique, showed high selectivity for C_4 hydrocarbons (over 50 mol%) with a conversion of less than 0.2% at 523 K (*2*, *3*). Klabunde *et al.* also showed that a Ni/MgO catalyst prepared in an analogous manner exhibited high activity for CO methanation when compared with a conventionally prepared catalyst (*4*).

Rieke *et al.* have published a sequence of reports concerning active metal powders generated by the reduction of metal halides with potassium metal in ethereal solvents, which have been used to synthesize new organic and organometallic compounds (*5*). We have initially reported (*6*) that Fe powders obtained according to Rieke's procedures showed excellent catalytic activity for F–T synthesis; 1-butene was obtained with greater than 30 wt% selectivity at a considerably high CO conversion (more than 10 wt%). In the present study, this catalytic system was characterized by conducting the reaction under various conditions; the variables were F–T reaction temperature, H_2/CO ratios, and different kinds of metal species used as the catalyst (Fe, Co, and Ni). We also carried out the F–T syntheses on composite metal powder catalysts, such as Fe–Co and Fe–Ni, since composite catalysts composed of these metal species have been reported (*7–9*) to

0021-9517/87 $3.00

show unique synergistic catalytic properties for F–T syntheses.

EXPERIMENTAL

Metal powder catalysts were prepared in a three-necked flask by the reduction of metal halides (FeI_2, $CoBr_2$, $NiBr_2$; 5.1×10^{-3} mol) with potassium metal (2.1×10^{-2} mol) in refluxing THF (150 ml) for 5 h under a flowing argon atmosphere. For binary metal powder preparation (Fe–Co and Fe–Ni), prescribed amounts of metal halides were added to the flask and reduced simultaneously by potassium metal. After the reduction, excess potassium was decomposed by methanol added dropwise to the flask. The synthesized black metal powders were collected by filtration and stirred in methanol (250 ml) for 30 min to remove KI or KBr that had been incorporated into the metal powders. All these procedures were performed in a dry nitrogen atmosphere. The metal powders thus obtained were dried at 383 K under vacuum overnight and used without delay.

A typical procedure for an F–T synthesis on the K-reduced metal powder catalyst was as follows: A 100-ml autoclave containing the metal powder catalyst (0.2 g) was flushed and filled with a mixture of CO and H_2 ($H_2/CO = 2.0$) up to 20 kg/cm^2 and electrically heated to 513–553 K. The time required to reach the reaction temperature was about 0.5 h. When the autoclave reached the prescribed temperature, it was immediately cooled by an air blast. We termed the reaction time of 0 min for this case. Such a condition was selected to supress any secondary reactions and was considered to represent the initial catalytic activity when the corresponding reaction was conducted in a flow reactor. Gaseous products were collected in a Pyrex vessel of a gas collecting apparatus. Oxygenates and hydrocarbons higher than C_8 were recovered, first, by evacuating the inside of the autoclave followed by washing with *n*-pentane. These products were analyzed by GC methods. The detailed procedures, such as the collection of products and GC analytical methods, have been previously described (*6*).

In all experiments, oxygenates, with the exception of water, were detected in trace amounts. Conversion to hydrocarbons, hydrocarbon product distribution, and olefin selectivity were estimated as follows: the weight percent of total hydrocarbons to all the materials recovered, the weight percent of a specific hydrocarbon to total hydrocarbons, and the weight percent of the olefin to a specific hydrocarbon, respectively. The olefins predominantly consisted of l-olefins.

BET surface areas of the K-reduced metal powders were measured by nitrogen adsorption using a conventionl Pyrex glass volumetric adsorption apparatus. The samples were evacuated at 473 K for 1 h prior to adsorption.

Surface features of the metal powders were observed using a scanning electron microscope (Hitachi S-450). The powders were attached to the sample holder with Ag paste. The KI or KBr content in the powder was determined by X-ray fluorometry (Rigaku Denki, Ultratrace-0600).

RESULTS AND DISCUSSION

F–T Syntheses under Various Conditions

Figure 1 shows the hydrocarbon product distribution at 553 K on the K-reduced Fe powder catalyst and a commercial Fe powder catalyst obtained by the thermal decomposition of $Fe(CO)_5$. A high selectivity for C_4 hydrocarbons is evident over the K-reduced Fe powder catalyst at the reaction time of 0 min, corresponding to ca. 42 wt% of the total hydrocarbons. In addition, C_4 hydrocarbons predominantly consisted of 1-butene (88% selectivity). The yields of CH_4 and hydrocarbons higher than C_6 were low. Thus, the K-reduced Fe powder catalyst produced C_2–C_5 hydrocarbons with high selectivity (79 wt%), which essentially consisted of 1-olefins (more than 80% selectivity). For comparison, the reaction was conducted under the same conditions on a

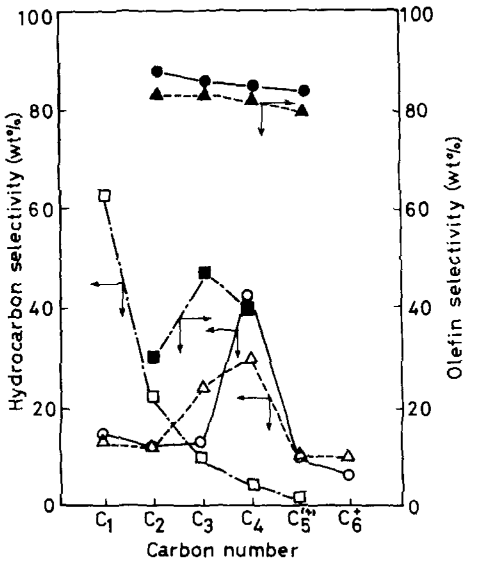

FIG. 1. Hydrocarbon product distribution and olefin selectivity on a K-reduced Fe powder catalyst and a commercial Fe powder catalyst made from $Fe(CO)_5$ at 553 K. A K-reduced Fe powder at 0 min (—) and 15 min (---) of F-T reaction time. A commercial Fe powder of 0 min (—·—) of F-T reaction time. Conversions were 11.7 (○) 16.2 (△) and 1.7 (□) wt%, respectively.

commercial Fe fine powder catalyst made from $Fe(CO)_5$ (Fig. 1). Conversion to hydrocarbons was only 1.7 wt%; less than one-fifth of that on the K-reduced Fe powder. The main hydrocarbon product was CH_4 while higher hydrocarbon yields decreased with increasing chain length. This suggests that the distinctive features of the K-reduced Fe powder catalyst is not due to the adopted reaction conditions but is due to its catalyses. Also, repeated reactions on the same K-reduced Fe powder catalysts, replacing only the feed gas in the autoclave, showed no deterioration in its selectivity (*6*). However, when the reaction time was extended to 15 min by using the K-reduced Fe powder as a catalyst (Fig. 1), selectivities for C_4 and olefins decreased considerably, although the CO conversion increased to 16.2 wt%. The reaction time of 0 min is adopted hereafter, since extention of reaction time causes secondary reactions.

Decreasing the temperature by 20 K to 533 K gave slightly better C_3–C_4 selectivity with somewhat higher olefin selectivity in the entire carbon number range, although a slight decrease (11.7 to 9.3 wt%) in percentage conversion was observed. Thus, the present Fe powder exhibits unique catalytic properties in this temperature region. At 513 K, only small amounts of hydrocarbons were detected. The Fe powder showed little catalytic activity at this lower temperature.

The feed gas composition (H_2/CO ratio) is also an important factor in F–T synthesis. Conventionally, lower H_2/CO ratios lead to higher olefin contents and longer chain hydrocarbons (*10*). Hydrocarbon product distribution obtained by changing the H_2/CO ratio from 2.0 to 1.0 at 553 K on the K-reduced Fe powder catalyst is shown in Table 1. Higher olefin selectivity was observed by increasing the CO content of the feed gas, reminiscent of products formed on general catalysts. In all the cases shown in Table 1, 1-butene was the main product and the conversion remained constant at 12 wt%. The largest amount of C_4 (45 wt% selectivity) was produced at a H_2/CO ratio of 1.5. At this ratio, the sum of the C_2–C_5 hydrocarbon yields was also the highest. Therefore, the preferable H_2/CO ratio to produce low-molecular-mass olefins, especially 1-butene, on the K-reduced Fe catalyst is 1.5.

It is also well known that Co is an effec-

TABLE 1

Effects of H_2/CO Ratio on F–T Products at 553 K Using K-Reduced Fe Powder as a Catalyst

H_2/CO ratio	Conversion (wt%)	Product distribution (wt%)					
		C_1	C_2	C_3	C_4	C_5	C_6^+
2.0	11.7	15	13 (88)[a]	13 (88)	42 (88)	11 (83)	7
1.5	11.9	10	14 (88)	15 (92)	45 (92)	12 (93)	4
1.0	11.8	13	18 (92)	19 (95)	30 (95)	13 (97)	7

[a] Olefin selectivity (wt%).

tive F–T catalyst (*10*). Accordingly, we have examined K-reduced Co powder catalysts prepared in a manner similar to that for the Fe powders. Hydrocarbon product distributions and olefin selectivities obtained on the Co catalyst at 513–553 K are given in Fig. 2. In contrast to the K-reduced Fe powder catalyst, products on the K-reduced Co catalyst showed little predominance for C_4 hydrocarbons and conventional Schulz–Flory type distribution (*10*); methane was obtained as the main product and yields of the higher hydrocarbons decreased as a function of C content. Lower olefin selectivity for the C_2–C_5 hydrocarbons (less than 45%) on the Co catalyst as compared to that on the Fe catalyst reflected relatively high Co hydrogenation activity (*10*). The lack of C_4 predominance on the Co catalyst implys that C_4 hydrocarbons, which are preferential products on Fe, do not originate from the THF used as the solvent for the preparation of the catalysts, but from the H_2 and CO feed gases. The features of the present Co catalyst are that only a small amount of hydrocarbons higher than C_6 is produced and that it exhibits catalytic activity even at 513 K, a temperature at which the K-reduced Fe catalyst showed little activity.

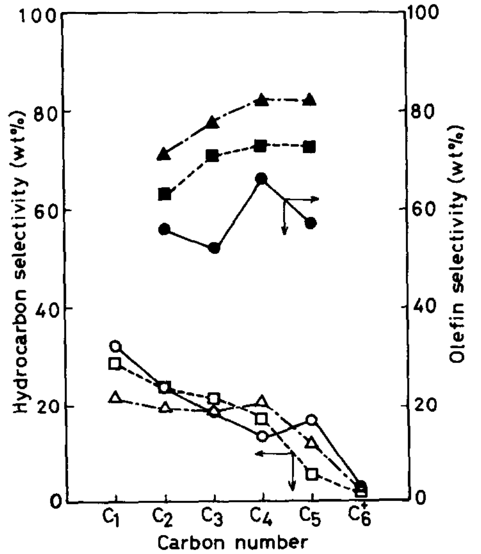

FIG. 2. Hydrocarbon product distribution and olefin selectivity on a K-reduced Co powder catalyst at 553 K (—) 533 K (---), and 513 K (—·—) with a H_2/CO ratio of 2.0. Conversions were 6.8, 6.4, and 4.4 wt% at 553, 533, and 513 K, respectively.

TABLE 2

Results of F–T Synthesis on a Fe–Co Binary Powder Catalyst of Varying Compositions[a]

Fe content (at.%)	Co content (at.%)	Conversion (wt%)	Product distribution (wt%)					
			C_1	C_2	C_3	C_4	C_5	C_6^+
0	100	6.8	32	19	19	15	13	2
				(27)[b]	(26)	(33)	(28)	
20	80	18.0	31	18	16	19	14	2
				(16)	(59)	(51)	(49)	
50	50	15.7	21	11	17	28	20	3
				(76)	(83)	(84)	(83)	
80	20	13.6	15	11	10	42	19	3
				(82)	(86)	(83)	(83)	
100	0	11.7	15	13	13	42	11	6
				(88)	(88)	(88)	(83)	

[a] F–T reaction conditions: 553 K; $H_2/CO = 2.0$.

[b] Olefin selectivity (wt%).

When Ni powders, prepared by the same procedures, are used as the F–T catalyst, they show no activity. This may be due to inactive carbonyl formation.

Binary metal catalysts, such as Fe–Co and Fe–Ni supported on TiO_2 have been reported to give higher CO conversions and higher selectivities for C_2–C_5 olefins than those on respective pure metal catalysts (*7*). An alloying agent (Co or Ni) of Fe is considered to make the iron carbide less stable (*7*). Accordingly, we have carried out the F–T syntheses on Fe–Co and Fe–Ni binary K-reduced powder catalysts expecting further improvements in the unique catalyses observed for the pure Fe powders.

The results of the F–T synthesis over a series of Fe–Co binary catalysts of varying compositions are summarized in Table 2. The reactions were carried out at 553 K with a H_2/CO ratio of 2.0. All the binary catalysts gave higher conversions than the pure Co or Fe catalysts, suggesting a synergistic catalytic activity. Maximum conversion was obtained at a composition of 20% Fe content. This result indicates that the binary powder catalysts prepared by the simultaneous reduction of the two metal halides are not simple mixtures of the respective metal powders. This observation is compatible with a previous report that catalysts prepared by impregnation by two different kinds of metal nitrates on TiO_2 followed by H_2 reduction have shown synergistic catalyses (7). Regarding the hydrocarbon distributions shown in Table 2, an increase in Fe content led to a decrease in CH_4 selectivity and an increase in olefin selectivity. The catalysts on Fe–Co (80 : 20) is most encouraging, since this catalyst shows higher conversion (13.6 wt%) and higher C_5 selectivity (19 wt%) than those on the pure Fe in spite of the equal C_4 selectivity, thus giving the largest amounts of C_4 + C_5 (61 wt% selectivity, 8.3 wt% yield) and C_2–C_5 (82 wt% selectivity, 11.2 wt% yield).

Accordingly, the catalytic character of this binary powder was studied in more detail. Figure 3 shows the effects of reaction temperatures. Behavior similar to that of the pure Fe powder was also observed on the Fe–CO (80 : 20) binary powder catalyst. Hydrocarbon distributions, olefin selectivities, and percent conversions changed only a little in the temperature region from 533 to 553 K. However, the unique catalysis character of the Fe–Co powder disappeared at 513 K. To suppress CH_4 formation and to further enhance 1-butene yield, the F–T synthesis on the Fe–Co (80 : 20) catalyst was conducted by using synthesis gas with a H_2/CO ratio of 1.0 instead of 2.0 at 553 K (Fig. 4). A slight increase in values of conversion (from 13.6 to 14.3 wt%), C_4 selectivity (from 42 to 43 wt%), and olefin selectivity (from 83 to 91 wt%) depended on the decrease in the H_2/CO ratio from 2.0 to 1.0 also resulting in a further increase in the 1-butene yield.

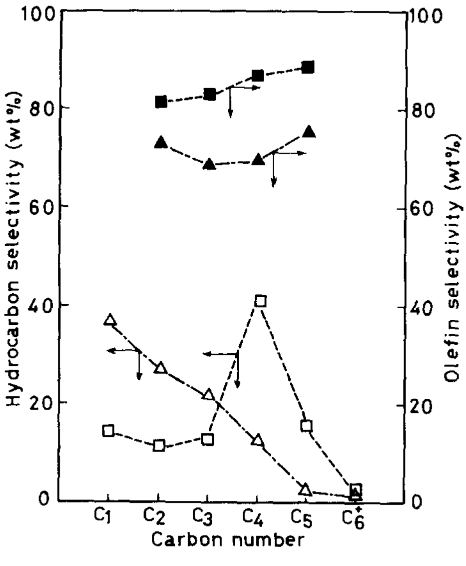

FIG. 3. Hydrocarbon product distribution and olefin selectivity on a Fe–Co (80 : 20) binary powder catalyst at 533 K (---) and 513 K (—·—) at a H_2/CO ratio of 2.0. Conversions were 12.3 and 1.9 wt% at 533 and 513 K, respectively.

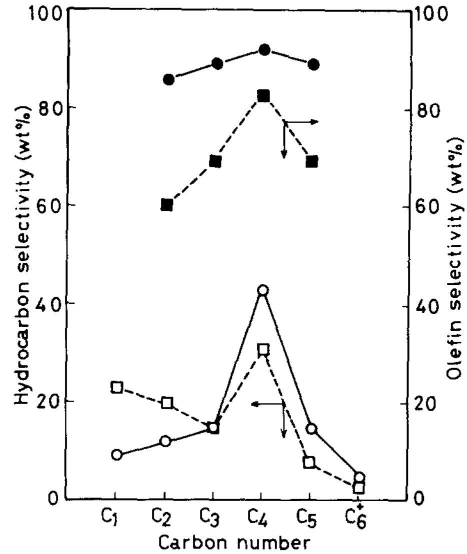

FIG. 4. Hydrocarbon product distribution and olefin selectivity on Fe–Co (80 : 20) (—) and Fe–Ni (80 : 20) (---) binary powder catalysts at 553 K with a H_2/CO ratio of 1.0. Conversions were 14.3 and 14.7 wt% on Fe–Co and Fe–Ni, respectively.

Figure 5 shows the results of F–T syntheses over a Fe–Ni (80 : 20) composite catalyst at 553 and 533 K with a H_2/CO ratio of 2.0. Above 533 K, this catalyst showed considerably high conversions of over 15.0 wt%, however, CH_4 was the main product with C_4 hydrocarbons in rather low yield. A higher temperature (553 K) led to an increase in conversion along with increased CH_4 selectivity and decreased olefin selec-

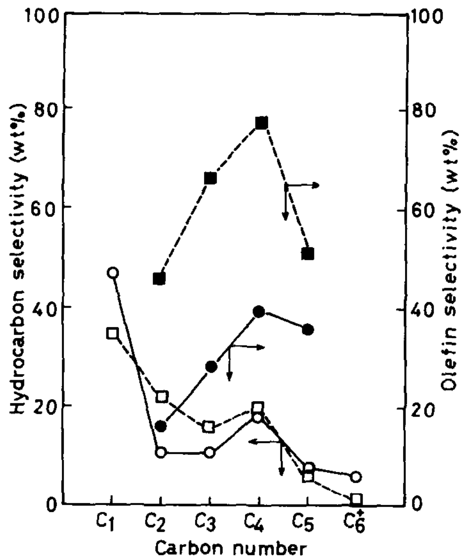

FIG. 5. Hydrocarbon product distribution and olefin selectivity on a Fe–Ni (80 : 20) binary powder catalyst at 553 K (—) and 533 K (---) with a H_2/CO ratio of 2.0. Conversions were 22.3 and 15.0 wt% at 553 and 533 K, respectively.

tivity. On the other hand, at 513 K, quite low catalytic activity was observed (conversion was 1.6 wt%). When the reaction was conducted with a H_2/CO feed gas ratio of 1.0 instead of 2.0 at 553 K (Fig. 4), CH_4 selectivity was reduced to 23 wt% and C_4 selectivity was improved to 30 wt%, although these values were inferior to those on the Fe or Fe–Co catalyst. Therefore, the composite catalyst of Fe containing Ni is inferior from the standpoint of selective 1-butene formation.

Characterization of Catalysts

BET surface areas of the K-reduced metal powders (Fe, Fe–Co (80 : 20), Fe–Co (50 : 50), and Co) are given in Table 3. The surface areas of these materials were 28–36 m^2/g, quite high for particles without support. This view was substantiated by a comparison of the BET surface area (4.3 m^2/g) of a commercial Fe powder prepared by the decomposition of $Fe(CO)_5$. From these data the radius of a K-reduced Fe powder may be estimated to be ca. 100 Å.

Scanning electron micrographs of the K-reduced Fe powder and the commercial Fe powder are shown in Fig. 6. One may observe for the K-reduced Fe powder that this very small powder stacks three dimensionally. The particle size determined by SEM was 250–90 Å, *in* accord with the one calculated by the BET surface area. The unique catalytic properties of the K-reduced metal powders may be at least partly due to its very small particle size distribution. Prevention of metal atom agglomeration by solvation of THF during the metal generation step results in the production of these small sized powders. The Co and Fe–Co (80 : 20) powders also observed by the scanning electron microscopy were very similar to the Fe powder.

A potassium derivative, such as K_2O or K_2CO_3, is frequently added as a promoter of catalysts for F–T syntheses (*10*). This compound has been theorized to donate electrons to the metal and accelerate CO dissociation (*10*). Even potassium halogenates, such as KBr and KCl, have been reported to act as promoters (*11*). Accordingly, the effects of KI and KBr need to be investigated, since these compounds are produced as by-products during the K reduction of the metal halides and are considered to contaminate the metal powder. F–T syntheses were conducted on K-reduced metal powder catalysts which contained two different amounts of potassium halogenates. They were prepared by one or three methanol washings. The results are shown in Table 4. The Fe, Fe–Co (80 : 20), and Co powders, used as the catalysts prepared by

TABLE 3

BET Surface Area of Various K-Reduced Metal Powders and a Commercial Fe Powder

Catalyst	BET surface area (m^2/g)
Fe	33.8
Fe–Co (80 : 20)	35.6
Fe–Co (50 : 50)	35.0
Co	28.0
Commercial Fe	4.3

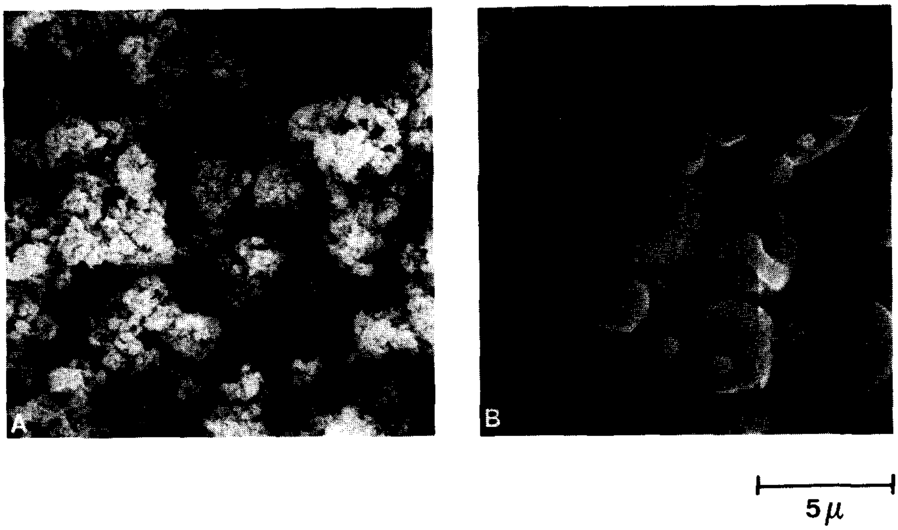

FIG. 6. Scanning electron micrograph of (A) a K-reduced Fe powder and (B) a commercial Fe powder made from $Fe(CO)_5$.

one washing, contained 3.8, 5.0, and, 6.1 wt% of KI or KBr. The content was less than 1.1% for catalysts prepared by three methanol washings. As is evident from the results in Table 4, conversions and hydrocarbon distributions using three types of powders changed only a small degree depending on KI or KBr content. Thus, we concluded that KI or KBr is not a significant factor during the unique catalyses of the present K-reduced metal powders.

TABLE 4

Effects of Amount of Potassium Halogenate in a K-Reduced Powder Catalyst on F–T Products[a]

Catalyst	KI or KBr content (wt%)	Conversion (wt%)	Product distribution (wt%)					
			C_1	C_2	C_3	C_4	C_5	C_6^-
Fe	3.8[b]	11.7	15	13 (88)[d]	13 (88)	42 (88)	11 (83)	6
Fe	0.7[c]	10.9	13	10 (85)	15 (87)	38 (88)	15 (88)	9
Fe–Co (80:20)	5.0[b]	13.7	15	11 (82)	10 (86)	42 (83)	19 (83)	3
Fe–Co (80:20)	0.8[c]	12.8	14	9 (84)	11 (86)	42 (88)	16 (87)	8
Co	6.1[b]	6.8	32	19 (27)	19 (26)	15 (33)	13 (28)	2
Co	1.1[c]	6.5	34	21 (23)	19 (25)	12 (36)	11 (28)	3

[a] F–T reaction conditions: 553 K; $H_2/CO = 2.0$.
[b] Prepared by one methanol washing.
[c] Prepared by methanol washings repeated three times.
[d] Olefin selectivity (wt%).

Origin of the unique catalytic properties of the K-reduced Fe and Fe–Co powders, especially concerning the high 1-butene selectivity, has not been clarified at present. The origins of this unique activity are presently under investigation by applying a variety of techniques. F–T syntheses by using a flow reactor with these catalysts are also under investigation.

REFERENCES

1. Fraenkel, D., and Gates, B. C., *J. Amer. Chem. Soc.* **102,** 2478 (1980).
2. Nazar, L. F., Ozin, G. A., Hugues, F., and Godber, J., *J. Mol. Catal.* **21,** 313 (1983).
3. Nazar, L. F., Ozin, G. A., Hugues, F., Godber, J., and Rancourt, D., *Angew. Chem. Int. Ed. Engl.* **22,** 624 (1983).
4. Klabunde, K. J., and Tanaka, Y., *J. Mol. Catal.* **21,** 57 (1983).
5. Rieke, R. D., *Acc. Chem. Res.* **10,** 301 (1977).
6. Nomura, M., Takebe, K., and Miyake, M., *Chem. Lett.* p. 1581 (1984).
7. Arai, H., Mitsuishi, K., and Seiyama, T., *Chem. Lett.*, p. 1291 (1984).
8. Stanfield, R. M., and Delgass, W. N., *J. Catal.* **72,** 37 (1981).
9. Amelse, J. A., Schwartz, L. H., and Butt, J. B., *J. Catal.* **72,** 95 (1981).
10. Dry, M. E. *In* "Catalysis" (J. R. Anderson and M. Boudart, Eds.), Vol. 1, p. 159. Springer-Verlag, New York, 1981.
11. Hammer, H., and Bitter, D., *Erdoel Kohle Erdgas Petrochem.* **31,** 361 (1978).