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Secondary Reactions on Metal–Zeolite Catalysts Used in Synthesis Gas Conversion[1]

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The mechanism of synthesis gas conversion over cobalt–ZSM-5 catalysts to gasoline-range hydrocarbons has been examined. A correlation exists between the methane yield and the percentage aromatics in the liquid hydrocarbon product. This could be due to heat transfer effects or to the hydrogenolysis of propane and butane over cobalt, leading to the formation of additional methane. The formation of additional alkanes (propane and butane) is known to accompany the aromatization process. The percentage of methane made by the bifunctional catalyst 4.2% Co/SiO_2 + ZSM-5 was 1.7 times that made by the Co/SiO_2 catalyst with a feed of $H_2/CO = 1$ at 280°C, 21 atm, and WHSV = 0.77. An attempt was made to inhibit secondary hydrogenolysis reactions by the addition of copper to the cobalt catalyst. Under similar process conditions, this provided a very small help in keeping down the increase in percentage of methane upon the addition of ZSM-5. Addition of 5 and 10% propane to the synthesis gas showed no additional methane made by hydrogenolysis. If indeed some of the methane produced over cobalt–ZSM-5 catalysts is coming from hydrogenolysis of light alkanes, it is a small amount.

INTRODUCTION

The catalytic conversion of synthesis gas to hydrocarbons over Fischer–Tropsch (FT) catalysts such as Fe and Co does not make liquid fuels with sufficient selectivity. The product distribution is governed by the Anderson–Schulz–Flory (ASF) polymerization kinetics (*1*); the maximum selectivity that could be obtained for the gasoline fraction (C_5–C_{11}) is 48% by weight of the total hydrocarbons formed. Olefinic and oxygenated products from FT synthesis can be converted over the medium-pore acidic zeolite H–ZSM-5 to gasoline-range hydrocarbons containing aromatics. In this manner, the FT products can be upgraded to yield high-octane gasoline. The method offers a possibility to circumvent ASF kinetics and obtain a gasoline-range product in excess of 48% of the total hydrocarbon product. The present paper will focus attention on the possible influence of secondary reactions on the metal surface in determining the selectivity of metal–zeolite catalysts.

Metal–zeolite catalysts made by combining an FT component with ZSM-5 have been examined in the conversion of synthesis gas (*2–11*). These combination catalysts provide a "nontrivial polystep" reaction (*12*) in which FT products are trapped and converted into aromatics, yielding a liquid hydrocarbon product of the high-octane-gasoline type directly from synthesis gas. Efforts have been made toward understanding the influence of the method of catalyst preparation on the conversion and selectivity. Of special interest is the possible correlation of the aromatization step with the additional methane formation. The objectives of the research are to (i) investigate mechanisms leading to methane formation by Fischer–Tropsch catalysts, (ii) compare routes to methane formation over metal–zeolite catalysts in single-stage and

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[1] Reference in this paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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two-stage conversions of syngas; and (iii) establish criteria to synthesize catalysts with reduced methane yield and examine the influence on liquid hydrocarbon yield and quality.

Previous investigations at this laboratory have examined cobalt–ZSM-5 catalysts that were prepared by three different methods (*9*): (i) direct decomposition of $C_5H_5Co(CO)_2$ on ZSM-5, (ii) impregnation of ZSM-5 with cobalt nitrate solution, and (iii) physical admixture of precipitated cobalt with ZSM-5. The physically admixed catalysts provided both a much higher fraction of aromatics in the liquid hydrocarbon product and a higher C_3 and C_4 saturate percentage than the solution- and organometallic-impregnated catalysts provide. In all cases, nearly 90% of the liquid hydrocarbon product was in the gasoline-boiling range. The percentage of C_3H_8 and C_4H_{10} in the product bore a direct correlation to the fraction of aromatics in the liquid hydrocarbon product. As explained by Dejaive *et al.* (*13*), the oligomerization of olefins is followed by aromatization that occurs through cyclization and hydrogen transfer reactions. The hydrogen transfer reactions lead simultaneously to the formation of saturated hydrocarbons (from olefins) and aromatics. Increased selectivity to aromatics, as in the case of the physically admixed catalyst, was accompanied by higher CH_4 yield and lower C_{5+} yield. The connection between the selectivities to aromatics and methane is the main subject of this paper.

Earlier work at this laboratory had shown (*7–9, 11*) that if the metal (Fe or Co) is impregnated directly on the ZSM-5, the metal interferes with the zeolite function. In this work, therefore, the metal-containing catalyst was prepared separately and was later physically admixed with the ZSM-5.

EXPERIMENTAL

1. Catalyst Preparation

a. Preparation of the metal component. The metal component (Co or Co–Cu) was prepared by two different methods: (i) the precipitation technique and (ii) the impregnation of amorphous silica with the metal nitrate solution.

(i) *Precipitation technique.* Cobalt oxide was initially made as a precipitate by adding a 10 wt% sodium carbonate solution at 70°C to a 10 wt% cobalt nitrate solution at 70°C until a pH of 7 was reached. The precipitate was filtered, washed with water thoroughly to reduce the content of sodium to less than 0.1 wt%, and dried at 110°C. The metal oxide with an average size of 5 μm by SEM was sieved to minus-200 mesh and then thoroughly mixed with Davison 952 silica with an average size of 70 μm. This mixture was later mixed with an equal weight of either silica or ZSM-5 and then pelleted.

(ii) *Impregnation technique.* Solution-impregnated catalysts were prepared by adding a cobalt nitrate solution to Davison 952 silica until incipient wetness was reached. The mixture was evacuated after the solution was added, and the final product was dried with stirring at 100°C. This product was later mixed with an equal weight of either silica or ZSM-5 and then pelleted.

b. Preparation of ZSM-5. The zeolite ZSM-5 was prepared according to the method given by Haag and Lago (*14*). The details of preparation are given below.

A sodium silicate solution was prepared by mixing 144.0 g of water and 249.3 g of N-brand sodium silicate (from the PQ Corp., 28.7 wt% SiO_2, 8.9 wt% Na_2O, 62.4 wt% H_2O). The solution was cooled to approximately 15°C. An acid solution was prepared by adding 10.1 g of aluminum sulfate $[Al_2(SO_4)_3 \cdot 18H_2O]$ to 147.6 g of water, followed by 21.6 g of sulfuric acid (97 wt% H_2SO_4) and 10.8 g of NaCl. These solutions were mixed together while 35.1 g of NaCl was added. In the starting gel, the SiO_2/Al_2O_3 molar ratio is 78.4.

The gel was placed in a stainless-steel liner inside a 2-liter Parr autoclave. The gel was stirred at 250 rpm while being heated to about 95°C. After 3½ hr the stirring was stopped. An organic solution containing 17.1 g of tri-*n*-propylamine, 14.4 g of *n*-propylbromide, and 27.9 g of methylethyl ketone was added above the gel. This mixture was held at 99–100°C for 16½ hr. Then stirring was resumed and the temperature was raised to 150–160°C and held there for 3 hr. The autoclave was removed for cooling, the solution was filtered, and the filter cake was washed with 20 liters of deionized water. After being dried at 110°C, the zeolite was calcined in air to 538°C at a rate of 2°C/min and held there for 16 hr. The zeolite was then ion exchanged for three 1½-hr periods with 5 wt% NH_4Cl (aq) (15 ml of NH_4Cl solution/1 g of zeolite) at 80°C. Washing was done on a filter funnel with 5 liters of water, and the zeolite was dried at 110°C.

The SEM measurements on the ZSM-5 prepared by the above method indicated that the crystallite size was in the range 0.1 to 0.5 μm.

c. Preparation of the catalysts. Metal–silica catalysts and metal–silica–zeolite catalysts were prepared from the above materials. All the components, except silica, were easily sieved through 200 mesh screens. The silica had an average particle size of 70 μm, nearly that of a 200 mesh screen. For the sake of comparing catalysts fairly, the metal loading of the precipitated catalyst (cobalt oxide physically admixed with silica) or of the impregnated catalyst (cobalt oxide impregnated on silica) was two times that desired for the final catalyst. Then 50% by weight of this cobalt/silica was mixed with 50% by weight of either silica or ZSM-5. All catalysts were pelleted before running in the microreactor. In the case of two-stage experiments, the cobalt–silica plus silica was pelleted and downstream of this was loaded the pelleted ZSM-5. An example of the nomenclature of the combined FT + ZSM-5 catalyst is 4.2% Co/SiO_2 + ZSM-5. This catalyst actually has 4.2 wt% cobalt/g catalyst; therefore the original impregnated catalyst was 8.4% Co on silica.

2. *Temperature-Programmed Desorption Studies*

Zowtiak *et al.* reported activated chemisorption behavior for supported and unsupported Co catalysts (*15*). The implication of such behavior is that surface areas obtained by static chemisorption measurements are a function of adsorption temperature and equilibration time. In an effort to estimate the optimum temperature for static chemisorption measurements, temperature-programmed desorption (TPD) studies were performed on the aqueous impregnated 12 wt% Co on silica catalyst sample.

The TPD instrument was similar in design to that of Lee and Schwarz (*16*). Linear heating rates (1–30°C/min) and isothermal control (±1°C) were obtained with this reactor configuration over a wide range of temperatures (25–750°C). The detector was a quadrupole mass spectrometer with mass range of 1 to 150 amu and unit mass resolution.

Approximately 0.1 g of the catalyst was heated at a rate of 10°C/min in a 100 ml/min stream of 5% H_2/N_2 to 450°C and held at that temperature in the reducing gas overnight (~18 hr). The sample was cooled to 40°C in the H_2 stream, and the TPD spectrum was obtained with a heating rate of 30°C/min to 450°C in a 100 ml/min flow of helium. Integration of the area under the H_2 desorption spectrum from 130 to 280°C gave the maximum H_2 chemisorption for the catalyst. Subsequently, the sample was cooled in flowing He to the selected adsorption temperature, T_a. While monitoring the reactor effluent stream, the sample surface was dosed with H_2 via the pulse loop until no more adsorption could be observed. The reactor was again cooled to 40°C, and a TPD spectrum obtained.

The hydrogen TPD spectra obtained in this manner from 12 wt% Co/SiO_2 at ad-

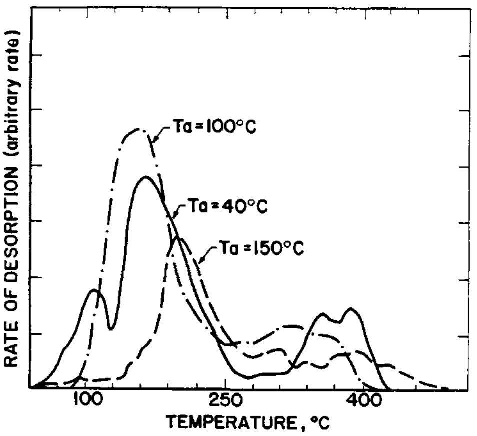

FIG. 1. Hydrogen TPD spectra from 12 wt% Co/SiO_2 subsequent to adsorption at three different temperatures (T_a = 40, 100, and 150°C).

sorption temperatures of 40, 100, and 150°C are shown in Fig. 1. Apparently, the adsorption was activated because the relative amount of chemisorbed hydrogen was greater at a T_a of 100°C than that at a T_a of 40 or 150°C, with the optimum adsorption temperature for static chemisorption near 100°C.

3. *Chemisorption Measurements*

Hydrogen chemisorption and oxygen titrations were performed by Micromeritics in the following manner. One gram of sample is loaded, and helium flows at 60 cc/min while the system is heated to 150°C at a rate of 4°C/min. In this way water is removed from the sample for 1 hr. The sample is pumped down for 2 hr at 150°C and then cooled. The reduction is carried out by flowing hydrogen at 60 cc/min while raising the temperature to 350°C at a rate of 2°C/min. The catalyst is reduced for 16 hr. Then the temperature is lowered to 340°C, and the sample is evacuated to 5×10^{-5} Torr for 2 hr. The sample is then cooled to 100°C under vacuum. Hydrogen is dosed in at 100, 200, 300, and 400 Torr. Following evacuation the dead space is measured with helium at 100°C.

Next the sample is evacuated to 5×10^{-5} Torr while the temperature is raised to 400°C at a rate of 4°C/min. Oxygen is dosed in at about 300, 350, and 400 Torr, and the uptake is measured. Following evacuation, the dead space is measured with helium at 400°C. The uptake of hydrogen extrapolated to 0 Torr gives the amount of total chemisorbed hydrogen. The uptake of oxygen at around 350 torr gives the micromoles of reduced cobalt titrated to Co_3O_4, and hence the percentage reduction of cobalt. The oxygen titrations showed that the catalysts were all nearly 100% reduced to cobalt metal.

4. *Catalytic Hydrogenolysis Experiments*

The propane hydrogenolysis results were obtained in a Chemical Data Systems continuous-flow microreactor. The feed gas was 77% helium, 20% hydrogen, and 3% propane. The fixed-bed, down-flow reactor used was constructed of 1-cm-i.d. stainless-steel tubing with a movable thermocouple inside a 1.5-mm-o.d. well to monitor the temperature along the 8-mm bed length. The outlet of the reactor was at 1 atm, with about a 10-psi pressure drop across the catalyst bed. Hydrogen was purified through a Deoxo trap followed by a molecular sieve trap. Mass flow meters delivered the correct flow rate of gases, and the product gas flow rate was measured by a wet test meter and a bubble meter. The inlet flow rate was 0.5 liter/min.

The product gas was sampled periodically and analyzed on a Hewlett–Packard 5730 gas chromatograph. The sample was simultaneously injected onto two columns. Hydrogen and helium were detected on a thermal conductivity detector (TCD) following separation on a molecular sieve column at 80°C with argon as the carrier gas. Methane and propane were detected on a TCD following separation on a Porapak column at 80°C with helium as the carrier gas. This GC system was calibrated using a standard consisting of 7.7% helium, 19.3% hydrogen, 2.7% propane, and 1.0% methane.

5. *Catalytic Conversion of Synthesis Gas*

Catalyst samples of 1.35 g were placed in a 1-cm-i.d., down-flow reactor tube. The catalyst was heated in flowing H_2 (70 ml/min) at 21 bar to 200°C at the rate of 2°C/min and held at that temperature for 1 hr. Subsequently, the temperature of the catyalyst was raised to 450°C (2°C/min) and held for 16 hr. The temperature was lowered to 250°C, and the pressure to 7 bar. Synthesis gas with a $H_2/CO = 1$ ratio was introduced, and then the pressure was slowly raised to 21 bar. The temperature was raised to 280°C, and a synthesis gas flow of 0.77 g/g cat. hr was maintained.

Some experiments were performed with the Fischer–Tropsch (FT) component separated from the ZSM-5 bed. The conversion was performed in two stages; the first stage consisted of the FT catalyst alone. It was separated by a layer of glass wool from the second bed, which consisted of ZSM-5 alone. Both catalyst beds were in one reactor tube. The temperatures of both beds were maintained at 280°C.

Two traps, maintained at 0 and 175°C, were used to collect the condensable products. Noncondensable product gas samples were analyzed for CO, H_2, CO_2, and C_1–C_7 hydrocarbons. The liquid that was drained from the trap at O°C was first weighed and then physically separated into aqueous and hydrocarbon fractions. The hydrocarbon product was analyzed by ASTM-D-2887 GC-simulated distillation. It was also separated into aromatics, olefins, and saturates by ASTM-D-1319 column chromatography with fluorescence indicator adsorption (FIA). Some samples with compositions given in Table 6 were also analyzed by dual capillary column analysis (*17*).

6. *Catalytic Conversion of Synthesis Gas plus Propane*

Several experiments were run with 5 and 10% propane premixed with 1 : 1 synthesis gas. As in the work of Kibby *et al.* (*18*), the gas hourly space velocity of synthesis gas was kept constant, while the total flow rate was higher when propane was added.

RESULTS AND DISCUSSION

1. *Single-Stage vs Two-Stage Conversions with Precipitated Cobalt and ZSM-5*

Experiments comparing the Fischer–Tropsch synthesis over a combined FT–ZSM-5 catalyst with that conducted in two sequential steps over separated FT and ZSM-5 catalyst beds have shed further light on the secondary reactions.

The FT catalyst tested was 14.4% precipitated cobalt physically admixed with Davison 952 silica. The average metal crystallite size, after reduction in hydrogen at 350°C, was determined from chemisorption measurements to be 35 nm. The conversion and selectivity of this catalyst are shown in the first column of Table 1.

The second column of Table 1 shows the results for the FT catalyst in the first stage and H–ZSM-5 in the second stage. Both stages were at 280°C. In this case, propene and butene are nearly totally involved in the production of aromatics, either as the building blocks in the oligomerization step or as the hydrogen acceptors in the aromatization step, where they would be converted to C_2–C_4 alkanes (*13*). The increase in the yield of C_3 and C_4 alkanes is noticeable, while the methane production is unchanged.

The third column of Table 1 shows the results for the FT catalyst mixed with H–ZSM-5 in a single stage. Of interest is the sharp increase in methane produced, while the weight percent of aromatics is nearly the same as that in the two-stage experiment. This suggests that a secondary reaction, possibly hydrogenolysis, is occurring over cobalt, resulting in the formation of additional methane from the light alkanes. The yield of C_2–C_4 alkanes is lower in this instance than in the two-stage experiment, thus supporting this hypothesis. This type of side reaction would be enhanced only in the single-stage experiment, where the ad-

TABLE 1

Conversion of Synthesis Gas in a Microreactor

Catalyst	14.4% Co/SiO_2 + SiO_2	14.4% Co/SiO_2 + SiO_2 (1st stage) ZSM-5 (2nd stage)	14.7% Co/SiO_2 + ZSM-5 (single stage)
CO conversion (%)	49.7	51.7	47.1
H_2 conversion (%)	79.8	80.5	83.0
HC product (wt%)			
CH_4	13.8	14.0	24.9
C_2H_4	0.2	0.1	0.2
C_2H_6	3.2	3.6	3.0
C_3H_6	4.8	0.0	0.4
C_3H_8	1.9	6.0	3.4
C_4H_8	2.5	0.0	0.9
C_4H_{10}	1.5	11.0	8.3
C_{5+}	72.1	65.3	58.9
Liquid product (wt%)			
Aromatics	3	33	35
Olefins	34	8	12
Saturates	63	59	53
C_{5+} breakdown			
Gasoline <204°C	37.2	60.9	52.1
Diesel 204–343°C	27.3	4.4	5.1
Heavies >343°C	7.7	0.0	1.7

Note. $H_2/CO = 1$, $P = 21$ atm, $T = 280°C$, WHSV = 0.77. Catalyst, precipitated cobalt with SiO_2. Cobalt crystallite diameter, ~35 nm.

ditional light paraffins can react over the cobalt particles in intimate contact with H–ZSM-5. Another possibility is that heat transfer effects are causing higher cobalt catalyst particle temperatures due to the addition of the highly exothermic aromatization reaction in the single-stage case.

2. *Single-Stage vs Two-Stage Conversions with Supported Co/SiO₂ and ZSM-5*

Chemisorption studies on solution-impregnated catalysts, reduced in hydrogen at 350°C, indicated that the average cobalt crystallite size was approximately 9 nm. Catalytic conversion tests were performed on the FT catalyst (4.3% Co/SiO_2), FT catalyst followed by H–ZSM-5 (two-stage reaction), and FT catalyst + H–ZSM-5 in a single bed. The results are shown in Table 2. The supported Co/SiO_2 shows a lower methane yield (9.2 wt%) than the precipitated cobalt catalyst (13.8 wt% methane yield) shown in Table 1. The supported Co/SiO_2 provides a gasoline-range product of 47.2 wt%, which is very nearly the upper limit predicted by the ASF polymerization kinetics. The addition of the zeolite component either in a two-stage reaction or in a single stage considerably increases the gasoline yield to 67.6 and 66.1%, respectively. In the case of the single-stage experiment with the FT–zeolite catalyst, the percentage of methane produced was considerably higher (14.9%) than the percentage produced by the two-stage reaction, FT catalyst followed by H–ZSM-5 (8.5%). This again suggests that either hydrogenolysis of the light alkanes or a higher cobalt catalyst temperature is causing additional formation of methane.

3. *Hydrogenolysis of Propane over Co–Cu Catalysts*

The specific activities of silica-supported Group VIII metals for hydrogenolysis of

TABLE 2

Conversion of Synthesis Gas

Catalyst	4.3% Co/SiO_2 + SiO_2	4.3% Co/SiO_2 + SiO_2 (1st stage) ZSM-5 (2nd stage)	4.2% Co/SiO_2 + ZSM-5 (single stage)
CO conversion (%)	47.4	44.6	55.5
H_2 conversion (%)	77.4	77.8	86.6
HC product (wt%)			
CH_4	9.2	8.5	14.9
C_2H_4	1.0	0.0	0.3
C_2H_6	2.1	2.3	1.9
C_3H_6	8.0	0.0	0.0
C_3H_8	0.0	5.1	3.1
C_4H_8	4.0	0.0	0.6
C_4H_{10}	0.5	10.7	6.6
C_{5+}	75.2	73.4	72.6
Liquid product (wt%)			
Aromatics	6	31	38
Olefins	52	8	16
Saturates	42	61	46
C_{5+} breakdown			
Gasoline <204°C	47.2	67.6	66.1
Diesel 204–343°C	22.2	5.8	6.4
Heavies >343°C	5.9	0.0	0.0

Note. $H_2/CO = 1$, $P = 21$ atm, $T = 280°C$, WHSV = 0.77. Catalyst, solution-impregnated Co/SiO_2. Cobalt crystallite diameter, ~9 nm.

ethane to methane, $C_2H_6 + H_2 \rightarrow 2\ CH_4$, at 205°C decrease in the following order (*19*):

$$\mathrm{Os > Ru > Ni > Rh > Ir > Re > Co > Fe > Cu > Pt \sim Pd.}$$

For the hydrogenolysis of propane, the sequence of activity is the following (*20*) (see Table 3):

$$\mathrm{Ru > Co > Ni > Fe.}$$

The approach to reduce the hydrogenolysis activity of cobalt was to alloy it with a second element of lower hydrogenolysis activity, such as Cu. In addition to altering the percentage *d*-character of the metallic bond, the alloying could be expected to result in the disruption of the surface ensemble of like atoms, resulting in a lowering of hydrogenolysis activity. Bimetallic catalysts Co–Cu/SiO_2 were prepared by aqueous impregnation and characterized using hydrogen chemisorption. Catalytic hydrogenolysis of propane on Co and the bimetallics was examined to investigate the change in specific activity with the addition of the second element. The addition of Cu results in a decrease in the specific activity for propane hydrogenolysis (see Table 4).

4. Syngas Conversion over Cobalt–Copper–ZSM-5 Catalysts

Bifunctional metal–zeolite catalysts cobalt–ZSM-5 and cobalt–copper–ZSM-5

TABLE 3

Relative Activities for Propane Hydrogenolysis at 280°C (*20*)

Catalyst	Activity[a]
Ru/alumina	4.86×10^3
Co/silica	4.03
Ni/silica	1.68×10^{-3}
Fe–Mg/silica	4.88×10^{-3}

[a] In units of μmol sec^{-1} (g cat)$^{-1}$ with hydrogen and propane pressures at 1.5 and 0.25 atm, respectively.

TABLE 4

Rate of Propane Hydrogenolysis ([Mol Propane Converted/h · m^2 of Metal] × 10^3)

Solution-impregnated catalyst	280°C	300°C	320°C
4.3% $Co/SiO_2 + SiO_2$	3.7	5.9	9.6
6.3% Co, 0.05% $Cu/SiO_2 + SiO_2$	2.5	4.7	7.1
5.0% Co, 0.3% $Cu/SiO_2 + SiO_2$	1.7	2.9	4.6

Note. WHSV = 5.0 g propane/g cat hr; propane conversion, ~10%.

were examined for the conversion of synthesis gas. The FT catalysts were prepared by the impregnation of SiO_2 with the metal nitrate solution and were then physically admixed with ZSM-5. The results for two 24-hr periods are shown in Table 5. The bifunctional catalyst 4.2% Co/SiO_2 + ZSM-5 made 1.7 times as much methane as Co/SiO_2 did with a feed of $H_2/CO = 1$ at 280°C, 21 atm, and WHSV = 0.77. Under similar process conditions, the catalyst 6.3% Co, 0.05% Cu/SiO_2 + ZSM-5 made 1.2 times as much methane as the catalyst 6.3% Co, 0.05% $Cu/SiO_2 + SiO_2$ did. Thus the addition of Cu to Co made some small difference in the additional methane formation. However, the catalyst 5.0% Co, 0.3% $Cu/SiO_2 + SiO_2$, which had the lowest propane hydrogenolysis activity in Table 4, produced 22 wt% methane. Not shown in Table 5, the bifunctional catalyst 5.0% Co, 0.3% Cu/SiO_2 + ZSM-5 produced 32 wt% methane in the first period. So instead of reducing the methane, this catalyst with a high copper loading increased the methane. This suggests that hydrogenolysis is less likely to be the cause of additional methane, since this catalyst has a very low rate of hydrogenolysis.

No work has appeared in the literature so

TABLE 5

Conversion of Synthesis Gas

	4.3% Co/SiO_2 + SiO_2		4.2% Co/SiO_2 + ZSM-5		6.3% Co, 0.05% $Cu/SiO_2 + SiO_2$		6.3% Co, 0.05% Cu/SiO_2 + ZSM-5	
Hours:	0–24	24–48	0–24	24–48	0–24	24–48	0–24	24–48
CO conversion (%)	47.4	40.3	55.5	47.5	40.8	33.7	63.1	54.8
H_2 conversion (%)	77.4	75.7	86.6	87.9	73.7	68.7	90.0	92.9
Product composition (wt%)								
CH_4	9.2	10.5	14.9	20.6	13.5	16.3	14.5	20.1
C_2-C_4	15.4	18.2	12.5	11.5	20.1	25.9	9.8	11.2
C_{5+}	75.4	71.3	72.6	67.9	66.4	57.8	75.7	68.7
Liquid hydrocarbon composition (wt%)								
Aromatics	0.0		19.0	13.4	0.0		8.4	6.6
Olefins	42.2		16.2	23.3	35.8		20.4	25.8
Saturates	47.0		41.2	37.6	51.3		35.5	26.6
Alcohols	5.3		0.0	0.0	5.4		0.0	0.0
Unknown	5.5		23.6	25.7	7.5		35.7	41.0
Co crystallite diameter (nm)	10.9		8.4		10.3			

Note. $H_2/CO = 1$, $P = 21$ atm, $T = 280°C$, WHSV = 0.77. Catalyst, solution-impregnated.

far with copper added to cobalt along with ZSM-5 for syngas conversion. However, studies show increases as well as decreases in the selectivity toward methane when copper was added to cobalt or nickel. Van Barneveld and Ponec (*21*) attempted to reconcile these differing results. They designed some experiments using mainly Ni–Cu unsupported catalysts and, in one case, a Co–Cu unsupported catalyst for the FT reaction. They concluded that both groups of authors were right. Alloying with Cu causes an increase in methane at temperatures below 275°C and a decrease in methane at higher temperatures.

5. *Heat Transfer Experiments over Supported Co/SiO$_2$ and Co/SiO$_2$ + ZSM-5*

One explanation for the additional methane in the single-bed FT + ZSM-5 case would be the presence of heat transfer effects. The addition of the highly exothermic aromatization reaction could have raised the catalyst particle temperature, thus leading to the increased percentage methane in the product. Several experiments were run following the experimental techniques developed by Madon and Boudart (*22*) for the Koros–Nowak criterion (*23*). This criterion is not obeyed when there are interphase or intraparticle heat or mass transfer effects. Madon and Boudart define $\rho = \bar{n}^0/(w\text{fw})$ where ρ is the active space velocity, $\bar{n}^0$ is the moles of reactant flow per second, w is the grams of catalyst, and fw is the weight fraction of the active material in the catalyst. If two experiments are performed and fw is changed but ρ is kept constant, the conversion will be the same when the Koros–Nowak criterion is obeyed.

The approach followed was to decrease fw to one-third of its original value and increase w threefold so ρ remained the same. The first sample was 1.35 g of a 4.3% Co catalyst (fw = 4.3%). The second sample was prepared by mixing one part of the previous catalyst powder with two parts by weight of Davison silica. The weight loaded into the reactor was three times that of the first. The synthesis gas conversion results are shown in Table 6. The CO and H$_2$ conversions were essentially the same as were the product distributions. Therefore, the conversion results on this catalyst obey the Koros–Nowak criterion and there are no heat transfer effects.

Analogous experiments with a 4.2% Co/SiO$_2$ + ZSM-5 catalyst were then carried out. Results with the undiluted catalyst were compared with those obtained with a mixture of one part of the catalyst with two parts silica, and the weight loaded into the reactor was three times that used with the undiluted catalyst. A second comparison was made with a mixture of one part 4.2% Co/SiO$_2$ + ZSM-5 with four parts silica. The weight loaded in this case was five times that of the first. However, in these tests, the CO conversion changed and the percentage methane decreased when the catalyst bed was diluted. The results are shown in Table 7. The conversion results on this catalyst do not obey the Koros–Nowak criterion suggesting that there are heat transfer effects in the undiluted catalyst. Also, in the catalysts diluted with silica, the percentage methane dropped to near 10%. This is perhaps the true percentage methane without any heat transfer effects. However, the catalysts mixed with silica gave few aromatics in the liquid product. This means less propane and butane were made in the hydrogen transfer reaction, so little methane could be expected from the hydrogenolysis route.

Perhaps the heat transfer effects caused hot spots in the cobalt and in the ZSM-5 for the unmixed 4.2% Co/SiO$_2$ + ZSM-5. This would explain the lower percentage methane and the lower percentage aromatics upon dilution. These tests do not conclusively rule out hydrogenolysis, because the diluted catalysts gave few aromatics and, thus, very little propane and butane. The pathway to methane suggested in this paper by way of hydrogenolysis requires a signifi-

TABLE 6

Conversion of Synthesis Gas in a Microreactor

Catalyst:	(4.3% Co/SiO_2 + SiO_2)		$\frac{1}{3}$(4.3% Co/SiO_2 + SiO_2) + $\frac{2}{3}$ SiO_2; 3× GMS	
Hours:	0–24	24–48	0–24	24–48
CO conversion (%)	47.4	40.3	52.6	37.1
H_2 conversion (%)	77.4	75.7	77.1	75.0
HC product (wt%)				
CH_4	9.2	10.5	10.3	11.7
C_2H_4	1.0	1.1	0.7	1.3
C_2H_6	2.1	2.4	2.4	2.7
C_3H_6	8.0	9.5	7.9	10.6
C_3H_8	0.0	0.0	0.0	0.0
C_4H_8	4.0	4.6	3.4	3.8
C_4H_{10}	0.5	0.6	0.4	0.0
C_{5+}	75.4	71.3	74.8	69.9
Liquid products (wt%)				
Aromatics	6	5	6	4
Olefins	52	57	48	56
Saturates	42	38	56	40

Note. H_2/CO = 1, *P* = 21 atm, *T* = 280°C, WHSV = 0.77. Catalyst, solution-impregnated.

TABLE 7

Conversion of Synthesis Gas in a Microreactor

Catalyst:	(4.2% Co/SiO_2 + ZSM-5		$\frac{1}{3}$(4.2% Co/SiO_2 + ZSM-5) + $\frac{2}{3}$ SiO_2; 3× GMS		$\frac{1}{5}$(4.2% Co/SiO_2 + ZSM-5) + $\frac{4}{5}$ SiO_2; 5× GMS	
Hours:	0–24	24–48	0–24	24–48	0–24	24–48
CO conversion (%)	55.5	47.5	64.2	47.5	61.4	43.5
H_2 conversion (%)	86.6	87.9	81.0	87.0	82.1	83.7
HC product (wt%)						
CH_4	14.9	20.6	10.4	11.0	9.5	11.5
C_2H_4	0.3	0.4	0.1	0.7	0.5	0.4
C_2H_6	1.9	2.5	2.1	2.4	2.4	3.4
C_3H_6	0.0	0.3	0.6	1.4	1.2	2.3
C_3H_8	3.1	2.6	1.9	1.4	1.5	1.4
C_4H_8	0.6	1.4	1.2	2.2	1.6	2.7
C_4H_{10}	6.6	4.3	3.8	2.9	2.3	3.2
C_{5+}	72.6	67.9	79.9	78.0	80.9	75.0
Liquid products (wt%)						
Aromatics	38	43	10	13	7	8
Olefins	16	22	59	67	72	73
Saturates	46	35	31	20	21	19

Note. H_2/CO = 1, *P* = 21 atm, *T* = 280°C, WHSV = 0.77. Catalyst, solution-impregnated.

TABLE 8

Conversion of Synthesis Gas and Propane

	50% H_2/50% CO		47.5% H_2/47.5% CO/ 5% C_3H_8		45% H_2/45% CO/ 10% C_3H_8	
Hours:	0–24	24–48	0–24	24–48	0–24	24–48
CO Conversion (%)	47.4	40.3	25.0	21.6	32.2	25.1
H_2 conversion (%)	77.4	75.7	58.3	45.0	64.7	52.2
HC product (wt%)						
CH_4	9.2	10.5	10.0	12.4	9.0	11.5
C_2H_4	1.0	1.1	0.6	0.8	0.5	0.7
C_2H_6	2.1	2.4	2.5	2.8	2.0	3.1
C_3H_6	8.0	9.5	7.2	10.0	5.7	8.6
C_3H_8	0.0	0.0	—	—	—	—
C_4H_8	4.0	4.6	5.0	6.6	3.8	5.7
C_4H_{10}	0.5	0.6	1.9	1.7	1.0	1.5
C_{5+}	75.2	71.3	72.8	65.7	78.0	68.9
Liquid hydrocarbon composition (wt%)						
Aromatics	0.0	—	0.0	0.0	0.0	0.0
Olefins	42.2	—	41.6	44.6	38.7	46.3
Saturates	47.0	—	49.1	43.5	50.1	41.4
Alcohols	5.3	—	4.7	6.9	4.2	6.3
Unknown	5.5	—	4.6	5.0	7.0	6.0
C_{5+} breakdown						
Gasoline <204°C	47.1	47.1	43.0	41.4	45.0	46.9
Diesel 204–343°C	22.2	19.4	22.6	18.4	23.4	17.2
Heavies >343°C	5.9	4.8	7.3	5.9	9.6	4.8

Note. H_2/CO = 1, P = 21 atm, T = 280°C, WHSV of H_2/CO = 0.77; over solution-impregnated catalyst, 4.3% Co/SiO_2 + SiO_2.

cant extent of reaction for the conversion to aromatics and a high percentage of propane and butane. Therefore, a more direct manner of testing, whether propane undergoes hydrogenolysis over cobalt under these operating conditions, was chosen. This was done by using synthesis gas mixed with 5 and 10% propane for conversion tests.

6. *Synthesis Gas plus Propane Conversion over Supported Co/SiO$_2$*

Catalytic conversion tests were performed on the supported Co/SiO_2 catalyst (4.3% Co/SiO_2) using 5 mol% and 10 mol% propane with 1 : 1 H_2 : CO. The results for two 24-hr periods are shown in Table 8. The supported Co/SiO_2 catalyst with synthesis gas alone produced approximately 10% methane as did the same catalyst with synthesis gas plus 5 or 10% propane. Thus, the addition of propane to the feed did not increase the level of methane formation. The CO conversion and H_2 conversion dropped when propane was added. This might be due to more surface coverage by adsorbed propane. This makes the idea of the possible hydrogenolysis of the light alkanes to methane over the FT catalyst + ZSM-5 in a single bed seem less likely.

7. *Discussion*

There appears to be no work reported in the literature of light alkane addition to synthesis gas. However, there can be some inferences drawn from the work on alkene addition. Kibby *et al.* (*18*) reported on the addition of ethylene and propylene to synthesis gas and its effect on conversion at 195°C. They found that over cobalt catalysts there were large increases in the yields of liquid hydrocarbons and a lower methane yield. Not all of this drop in methane could be attributed to the decrease in hydrogen partial pressure with added olefin. Also, the chain growth probability for C_{5+} was lowered by olefin addition. This was attributed to chain termination by the added olefin. In comparison, the results from this laboratory did not show any change in the product selectivity with additional propane. One explanation might be that ethylene and propylene would be expected to adsorb more readily than propane and then to undergo further reaction. However, the carbon monoxide and hydrogen conversions were decreased by the addition of propane. There was probably some additional surface coverage by the propane. This present work shows no real increase in the amount of methane upon addition of propane, an increase that would be expected if hydrogenolysis were occurring to a significant extent.

Some authors (*24*) have suggested that hydrogenolysis of the light alkenes over iron and cobalt catalysts is unlikely to be important due to the competitive adsorption of CO on the metal sites. On the other hand, Jordan and Bell (*25*) have shown that hydrogenolysis of ethylene and propylene occurs over ruthenium/silica catalysts. When they added 0.035 atm C_3H_6 to 0.40 atm H_2/0.20 atm CO at 220°C, the addition inhibited methane formation, mainly by reducing the rate of formation of methane from ^{13}CO. However, some methane was still coming from the hydrogenolysis of unlabeled propylene. Also, the conversion of CO to hydrocarbons dropped, which we also observed with added propane.

Recalling the data from Table 3, the rate of propane hydrogenolysis was greatest over ruthenium, less over cobalt, and least over iron. One might expect that propane hydrogenolysis in the presence of hydrogen and carbon monoxide is likely because of Jordan and Bell's propylene work. One might also expect that propane hydrogenolysis is somewhat likely over cobalt and least likely over iron. The experiments performed in this laboratory did not indicate whether hydrogenolysis of light alkanes is occurring over cobalt. They did show that the overall percentage of methane formed remains the same in the presence of added propane. Some ^{13}CO and unlabeled C_3H_8 experiments alone would tell whether hydrogenolysis of light alkanes does occur over cobalt in the presence of hydrogen and carbon monoxide.

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