SYNGAS CONVERSION AND CHEMISORPTION STUDIES ON METAL-ZEOLITE CATALYSTS

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Cobalt-ZSM-5 and cobalt-thoria-ZSM-5 catalysts have been examined for synthesis gas conversion at 280°C. In the cobalt-ZSM-5 catalysts prepared by the impregnation of ZSM-5 with cobalt nitrate solution, it was shown by chemisorption and magnetization studies that the amount of cobalt that could not be reduced to metallic form in flowing H_2 at 350°C amounted to nearly 2 wt% of the catalyst, and evidently was ion-exchanged. Cobalt-ZSM-5 catalysts prepared via the physical admixture of precipitated cobalt oxide with ZSM-5 were also examined. In synthesis gas conversion and in ethylene conversion, the physically admixed catalysts showed a higher fractional yield of aromatics in the liquid hydrocarbon product than the solution-impregated catalysts. Catalysts prepared by the impregnation of ZSM-5 with $C_5H_5Co(CO)_2$ and containing 3 [illegible] cobalt showed higher metal dispersion, higher H_2 + CO conversion, and about 10 times higher yield of gasoline range hydrocarbons (g/hr) than the catalysts with similar metal loading prepared by the other two methods. Addition of thoria as a promoter to cobalt-ZSM-5 caused a considerable increase in synthesis gas conversion and selectivity to gasoline-range hydrocarbons. Some Co-ThO_2-ZSM-5 catalysts provided, during the first 24-hour period of the test, nearly 65 wt% selectivity to gasoline-range product that contained 26 vol% aromatics (alklbenzenes). Addition of thoria resulted in the decrease of the cobalt crystallite size from about 40 nm to 10 nm, and caused an increase in CO/H adsorbed. The conversion of synthesis gas in a single stage metal-zeolite catalyst has been compared over that in a dual stage set-up with separated Fischer-Tropsch and zeolite catalysts.

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The narrative account of the presentation "Syngas Conversion and Chemisorption Studies on Metal-Zeolite Catalysts" by V. Udaya S. Rao can be found in the manuscripts that have been included in addition to a copy of the slides. The manuscripts are:

(1) "Zeolite-Supported Cobalt Catalysts for the Conversion of Synthesis Gas to Hydrocarbon Products" by A. Shamsi, et al.

(2) "Promotion and Characterization of Zeolitic Catalysts Used in the Synthesis of Hydrocarbons from Syngas" by V. U. S. Rao, et al.

SCOPE OF WORK

1. Prepare Co-ZSM-5 catalysts by three different methods.
   - a. Physical admixture of precipitated cobalt oxide with HZSM-5.
   - b. Impregnation with metal nitrate solution.
   - c. Direct decompostion of $C_5H_5Co(CO)_2$ on HZSM-5.

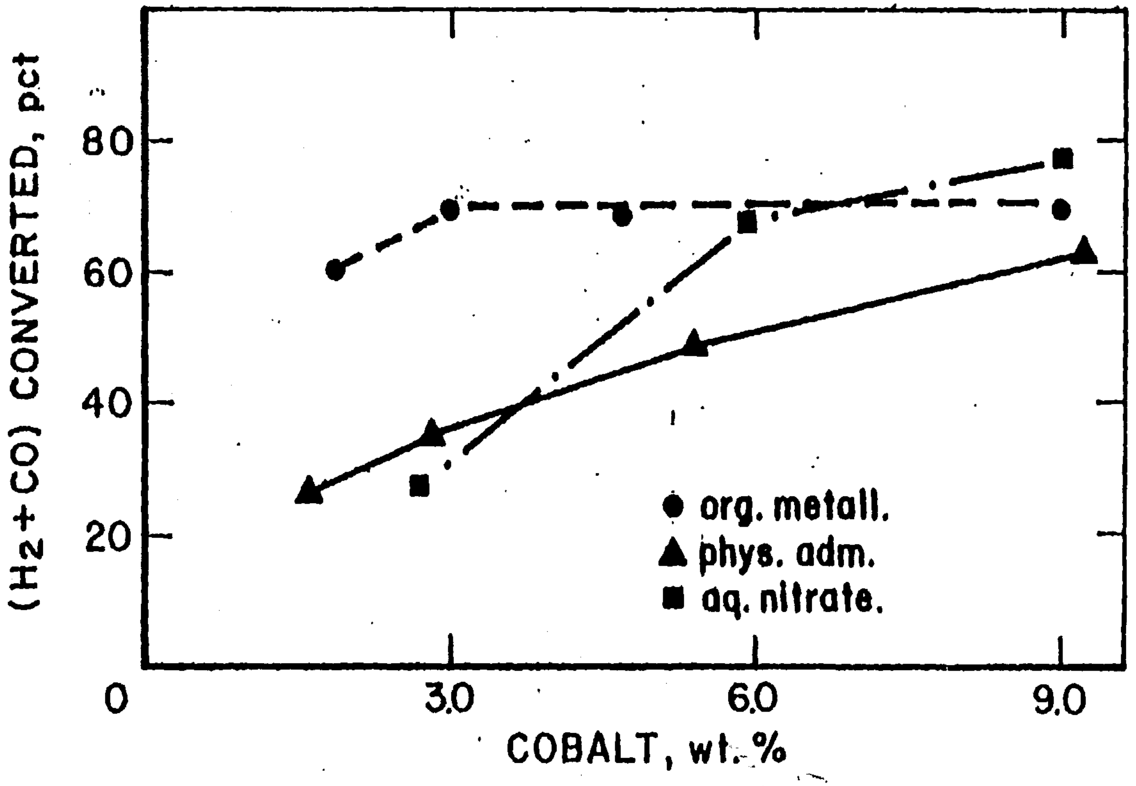
2. Study catalytic activity and selectivity of these catalysts for the conversion of synthesis gas to hydrocarbon products.

3. Examine the influence of thoria as a promoter on Co-ZSM-5.

4. Determine metal dispersion using chemisorption and magnetization studies.

5. Relate degree of dispersion of metal component to the preparation procedures and catalytic properties.

6. Preliminary investigation to compare single stage and two-stage conversion over FT/ZSM-5 catalysts.



Catalytic activity versus the weight percent cobalt for the series of cobalt-ZSM-5 samples.

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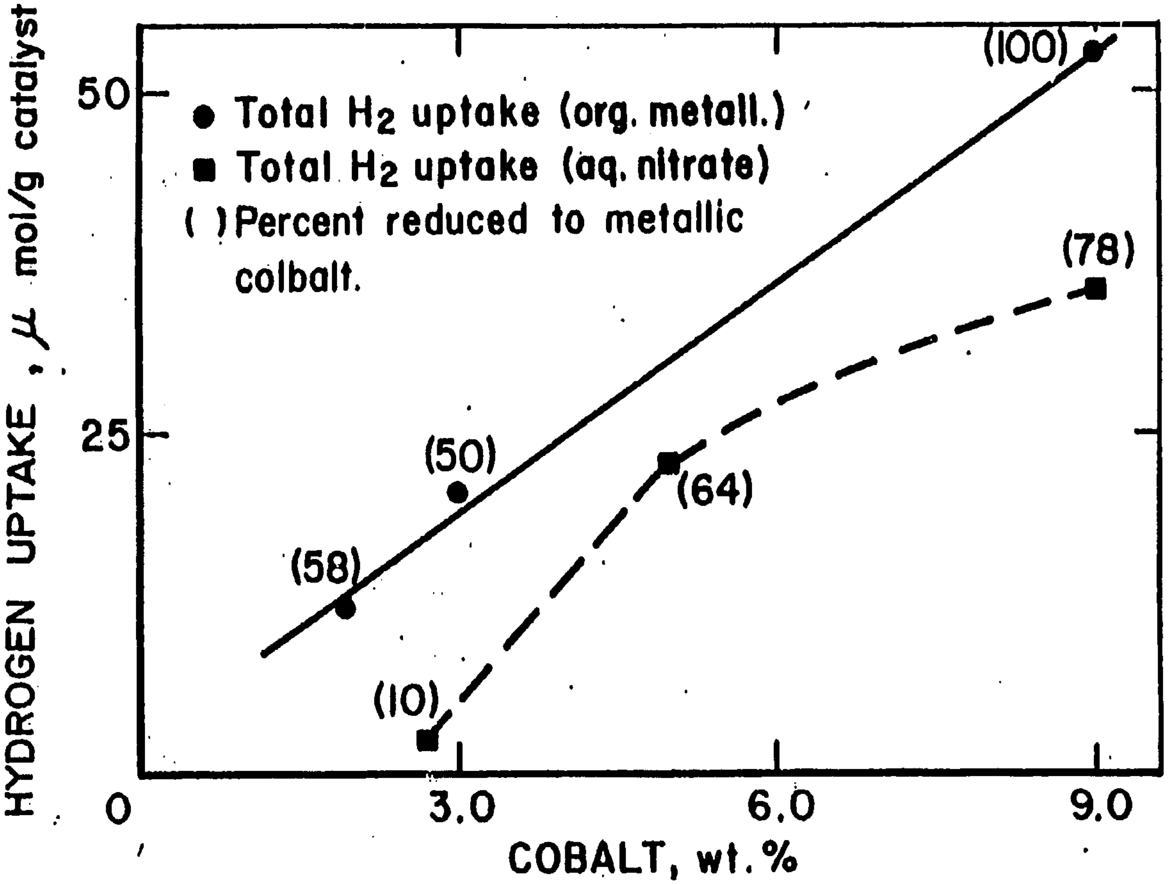

Total H_2 uptake versus metal loadings.

BSI/3793

Micrcreactor Results
$H_2/CO = 1$, P = 21 atm, T = 280°C, WHSV = 0.77
(0-24 hour period)

	3.0% Co/ZSM-5 (organometallic impregnation)	2.7% Co/ZSM-5 (metal nitrate impregnation)	2.8% Co/ZSM-5 (physical mixture)
Co crystallite size (nm)	5	8	
CO Conversion (%)	52.9	21.0	24.8
H_2 Conversion (%)	85.2	34.3	46.0
Product Composition (wt.%)			
CO_2	11.7	8.1	10.4
H_2O	52.5	56.6	53.7
CH_n	35.9	35.3	35.9
Composition of CHn (wt%)			
CH_4	23.5	33.5	32.5
C_2H_4	0.0	0.0	0.0
C_2H_6	2.7	5.2	3.4
C_3H_6	0.0	0.0	0.0
C_3H_8	4.0	7.7	12.5
C_4H_8	1.2	0.9	0.0
C_4H_{10}	6.5	18.8	23.0
C_{5+}	62.1	33.9	28.6
Liquid Product Composition (vol%)			
Aromatics	13.0	—	—
Olefins	44.5	—	—
Saturates	42.5	—	—

Microreactor Results
$H_2/CO = 1$, $P = 21$ atm, $T = 280°C$, WHSV = 0.77
(0-24 hour period)

	9.0% Co/ZSM-5 (organometallic impregnation)	9.0% Co/ZSM-5 (metal nitrate impregnation)	9.2% Co/ZSM-5 (physical mixture)
Co crystallite size (nm)	10	12	43
CO Conversion (%)	53.5	56.5	47.5
H_2 Conversion (%)	86.5	85.9	78.0
Product Composition (wt.%)			
CO_2	10.1	18.6	8.5
$_2O$	53.7	46.1	53.8
CH_n	36.3	35.2	37.7
Composition of CHn (wt%)			
CH_4	17.7	24.5	26.5
C_2H_4	0.0	0.0	0.0
C_2H_6	2.0	2.7	1.6
C_3H_6	1.2	0.85	0.0
C_3H_8	1.8	2.7	6.1
C_4H_8	1.0	0.7	0.6
C_4H_{10}	2.0	5.4	13.8
C_{5+}	74.3	63.1	51.4
Liquid Product Composition (vol%)			
Aromatics	13.5	22.0	50.5
Olefins	63.5	31.0	6.5
Saturates	23.0	47.0	43.0

Chemisorption of H_2 on Co-ZSM-5 Prepared by Aqueous Nitrate impregnation

Metal Loading (wt%)	% Reduction in H_2 at 350°C	Wt% Co Unreduced	H_2 Uptake at 100°C (μ mol g^{-1})	d(nm)
9.0	78	2.0	35.4	12.4
5.9	64	2.1	22.5	10.5
2.7	10	2.5	2.5	7.0

Catalytic tests on Co-ThO_2-HZSM-5 with $H_2/CO = 1$, $P = 21$ bar, $T = 280°C$, WHSV = 0.66

(0-24 hour period)

Co in catalyst (wt%)	9.2	8.8	8.5	8.9
ThO_2 in catalyst (wt%)	0.0	0.4	0.8	1.5
CO conversion %	47.5	67.1	71.1	74.0
H_2 conversion %	78.0	88.1	89.0	91.6
Composition of Hydrocarbon Product (wt%)				
CH_4	26.5	19.4	16.1	16.4
C_2H_4	0.0	0.0	0.1	0.1
C_2H_6	1.6	2.6	2.0	1.7
C_3H_6	0.0	0.0	0.2	0.3
C_3H_8	6.1	3.9	3.4	2.9
C_4H_8	0.6	0.9	0.8	0.7
C_4H_{10}	13.8	6.0	6.1	5.4
C_{5+}	51.4	67.2	71.4	72.5
Liquid Product Composition (vol%)				
Aromatics	50.5	18.5	21.5	20.0
Olefins	6.5	48.0	39.5	44.5
Saturates	43.0	33.5	39.0	35.5

Chemisorption Results on Co-ZSM-5 and Co-ThO_2-ZSM-5 Catalysts

Catalyst Composition (wt%) Cobalt	Thoria	Degree of Reduction (%)	Gas Uptake[a] (μ mole g^{-1}) CO at 25°C	H_2 at 100°C	$\frac{CO}{Co}$	$\frac{H}{Co}$	$\frac{CO}{H}$	d^b (nm)	d^c (nm) (I)	(II)
9.2	0.0	98	16.4	13.2	0.0107	0.0173	0.62	42.3	34.4	68.8
8.5	0.8	92	56.3	33.3	0.0424	0.0502	0.84	14.7	8.7	17.4
8.9	1.5	80	70.3	34.0	0.0501	0.0563	1.03	13.1	6.3	12.6

[a] Irreversible CO adsorption and total H_2 adsorption

[b] Based on total H_2 adsorption, assuming $H/Co_s = 1.0$

[c] Based on irreversible CO adsorption, assuming (I) $CO/Co_s = 0.5$ and (II) $CO/Co_s = 1.0$

Single stage versus two-stage synthesis.
F-T catalyst: Precipitated cobalt-thoria
$H_2/CO = 1$, $P = 21$ bar, $T = 280°C$, $WHSV = 0.66$

Catalysts:			
1st stage:	F-T + silica	F-T + silica	F-T + HZSM-5
2nd stage:	none	HZSM-5	none
CO conversion %	65.9	65.7	74.0
H_2 conversion %	78.0	79.9	91.6
Composition of Hydrocarbon Product (wt%)			
CH_4	19.5	18.9	16.4
C_2-C_4	13.5	23.6	11.2
C_{5+}	67.0	57.5	72.4
% gasoline in C_{5+}	57	97	98
Liquid Product Composition (vol%)			
Aromatics	3.5	22.5	20.0
Olefins	36.5	7.0	44.5
Saturates	60.0	70.5	35.5

CONCLUSIONS

1. At about 3 wt. % metal loading, Co-ZSM-5 catalyst prepared from decomposition of $C_5H_5Co(CO)_2$ showed higher metal dispersion, (H_2 + CO) conversion, and about 10 times higher yield of gasoline range hydrocarbons (g/hr) than the catalysts prepared by impregnation with metal nitrate solution or by the physical admixture method.

2. Addition of thoria to cobalt-ZSM-5 results in the decrease of cobalt crystallite size from 42 nm to 13 nm. Cobalt-thoria-ZSM-5 catalysts can yield nearly 70 wt% of the hydrocarbon product in the gasoline range, exceeding the limitations to selectivity (48%) imposed on conventional F-T catalysts by Schulz-Flory kinetics.

3. Preliminary experiments show significant difference in selectivity between single stage and two-stage conversion over Co-ThO_2/ZSM-5.

ZEOLITE-SUPPORTED COBALT CATALYSTS FOR THE CONVERSION OF SYNTHESIS GAS TO HYDROCARBON PRODUCTS

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Abstract

Three differently prepared cobalt/ZSM-5 catalysts were investigated with respect to physical and chemical properties and to activity and selectivity for conversion of synthesis gas. The catalyst preparations consisted of the following: (1) direct decomposition of $C_5H_5Co(CO)_2$ on ZSM-5, (2) impregnation of ZSM-5 with an aqueous solution of cobalt nitrate, and (3) physical admixture of precipitated cobalt oxide with ZSM-5. The concentration of cobalt varied from 1.5 wt% to 9 wt%. At about 3 wt% cobalt loading, the first catalyst showed higher dispersion, higher (H_2 + CO) conversion, and about 10 times higher yield of gasoline-range hydrocarbons (g/hr) than the catalyst prepared by the other two methods. Some H_2 and CO chemisorption studies and magnetization measurements were conducted to measure the average particle diameter. The CO/H adsorption ratio is lower for the catalyst prepared from $C_5H_5Co(CO)_2$ than for the catalyst from the metal nitrate solution. This ratio increases with increasing metal dispersion. At low metal loading, the organometallic-impregnated catalyst has a higher degree of reduction and hydrogen uptake compared to the solution-impregnated catalyst. Infrared studies of chemisorbed pyridine on these samples indicate that ion exchange of Co^{2+} for acidic protons occurs in organometallic-impregnated and aqueous-solution-impregnated catalysts; however, the extent of ion exchange is greater for catalysts prepared by the latter technique. No ion exchange is found in physically admixed catalysts. In addition, the infrared data suggest that the organometallic preparation can cause blockage of the ZSM-5 channels unless appropriate activation procedures are followed.

1. Introduction

The medium-pore zeolite ZSM-5 can catalytically convert methanol or other oxygenates to hydrocarbons containing aromatics (Chang and Silvestri, 1977). It has been proposed that the acid function of ZSM-5 is responsible for the catalytic synthesis of aromatics (Derouane and Vedrine, 1980). The ZSM-5 has uniform pores of about 5.5-Å diameter governed by a 10-membered oxygen ring opening that results in a sharp cutoff in the aromatic product distribution at C_{10} (Chang and Silvestri, 1977).

Olefins can be oligomerized by ZSM-5 to heavier olefins, followed by isomerization, cyclization, and aromatization (Dejaive et al., 1980) to form a gasoline-range product. The liquid product contains branched paraffins, branched olefins, naphthenes, and aromatics, which are constituents of high ctane gasoline.

Since products of synthesis gas conversion by the Fischer-Tropsch reaction contain olefins and oxygenates, there is considerable interest in combining a Fischer-Tropsch metal, such as Fe, Co, or Ru, with ZSM-5 to form a bifunctional catalyst. These catalysts exhibit improved selectivity for a gasoline-range product, and synthesis gas can be converted to gasoline-range hydrocarbons in one step (Chang et al., 1979; Caesar et al., 1979; Rao and Gormley, 1980).

The activity, stability and product selectivity of supported catalysts can be significantly affected by the properties of the support and the method of preparation. For example, catalysts prepared from the transition metal carbonyls or organometallics showed a higher degree of dispersion of metal on the support than the catalysts prepared from the aqueous solution of the high-valent salt (Brenner, 1975; Thomas et al., 1982). It was of interest to examine if the former methods could be employed to prepare zeolite-supported catalysts.

Our investigation was undertaken in an attempt to increase the metal dispersion on cobalt/ZSM-5 catalysts using organometallics as the source of cobalt and to compare with the conventional methods of catalyst preparation. Catalysts were prepared in three different ways: (1) decomposition of dicarbonylcyclopentadienylcobalt on ZSM-5, (2) impregnation of ZSM-5 with cobalt nitrate solution, and (3) physical admixture of precipitated cobalt oxide with ZSM-5. The catalysts were tested in a microreactor for the conversion of synthesis gas ($H_2/CO = 1$) at 280°C, 21 atm, and WHSV = 0.77. Metal dispersion was measured using chemisorption and magnetization studies. The possible relationship between the degree of dispersion and the catalytic activity was examined. Infrared spectroscopy was used to investigate the influence of the preparation method on the relative number of Brōnsted and Lewis acid sites.

2. Experimental

(a) Catalyst Preparation:

The ZSM-5 with SiO_2/Al_2O_3 ~30 was prepared using the procedure described in the patent literature (Argauer and Landolt, 1972). The preparation yields ZSM-5 crystallites of approximately 1μ. The zeolite was calcined in air at 538°C to decompose the TPA+ and ammonium-exchanged using NH_4Cl solution. The ammonium form of ZSM-5 was then calcined in air at 538°C to obtain the acid form of ZSM-5.

The organometallic-impregnated catalysts were prepared by decomposing $C_5H_5Co(CO)_2$ on ZSM-5 in an evacuated sealed glass bulb. The cobalt content of the catalyst was determined by atomic absorption (AA) techniques.

Solution-impregnated catalysts were prepared by adding a cobalt nitrate solution to ZSM-5 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.

For the physically admixed preparation, cobalt oxide was initially made as a precipitate by adding a 10 wt% sodium carbonate solution at 70°C to a second solution, also at 70°C, containing 10 wt% cobalt nitrate 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 dried zeolite and metal oxide were each sieved to -200 mesh and thoroughly mixed.

(b) Chemisorption Measurement:

Hydrogen and carbon monoxide adsorption measurements were carried out to measure the metal dispersion. Adsorption measurements were performed using a conventional glass volumetric adsorption apparatus. One gram of each catalyst was used in the measurements. The sample was heated to 200°C (2°C/min) under flowing He (60 mL/min) and kept at that temperature for

1 hr. The sample chamber was then evacuated to 2×10^{-5} torr before cooling to 50°C. At this temperature, hydrogen was introduced (60 mL/min) and the temperature was raised to 350°C (2°C/min). The sample was reduced at this temperature for 18 hr. Reduced samples were evacuated to 2×10^{-5} torr at 340°C and cooled to the adsorption temperature.

Hydrogen adsorption was performed and adsorption isotherms were obtained at 100°C. The H_2 uptake value at the zero pressure intercept corresponds to saturation coverage of adsorbed H_2 on the metal at that temperature. Total H_2 uptake was used to calculate the metal dispersion and crystallite size.

Following the H_2 adsorption measurement, the catalyst chamber was evacuated and the sample was reduced under flowing H_2 (60 mL/min) for 1 hr at 350°C. The sample was evacuated to 2×10^{-5} torr at 340°C and cooled to 25°C for CO adsorption measurements. Two isotherms were obtained assuming that the initial isotherm represents the sum of CO strongly adsorbed on the metal and weakly bound to the support. Evacuation of the sample at 25°C to 2×10^{-4} torr for 0.5 hr prior to measurement of the second isotherm removes weakly adsorbed CO. The difference between the two isotherms at the zero pressure is taken to represent the irreversible adsorption of CO on the cobalt surface.

The magnetic measurements were performed on a reduced sample (350°C and flowing H_2 for 16 hr) using a vibrating sample magnetometer in an applied field up to 15 kOe. The saturation magnetization was measured by plotting σ versus $1/H$ and extrapolating to zero (infinite fields), assuming that small magnetic particles have the same saturation magnetization as bulk material (Selwood, 1975). The degree of reduction was obtained by comparing the values obtained with the known saturation magnetization of bulk cobalt.

(c) Infrared Studies:

Samples for infrared spectral measurement were prepared by pressing approximately 20 to 30 mg of the catalyst into thin wafers using a ½-inch die. The wafers were mounted on a quartz sample holder and installed into a quartz pyrex vacuum system, similar to that described by Rhee et al. (1983). The IR data were obtained on reduced and calcined samples. The wafer was reduced with flowing H_2 at 350°C for 2 hr. After evacuation, pyridine was adsorbed at 150°C. The same procedure was followed after O_2 calcination at 450°C. Spectra were recorded using a Perkin-Elmer Model 180 infrared spectrophotometer. The frequencies reported herein are accurate to within ±2 cm^{-1}, while the precision of intensity ratios is approximately ±15%.

(d) Synthesis Gas Conversion:

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 catalyst was raised to 350°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 the $H_2/CO = 1$ ratio was introduced and 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.

Two traps, maintained at 0°C and 175°C, respectively, were drained periodically at 24-hr, 48-hr, or 72-hr intervals. Product gas samples were analyzed for CO, H_2, CO_2, and C_1-C_7 hydrocarbons. The liquid drained from the trap at 0°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). The amount of product collected in the trap at 175°C was negligible.

3. Results and Discussion

(a) Catalyst Characterization:

The present investigations on cobalt/ZSM-5 catalysts prepared by three different methods (mentioned before) had the following aims: (a) investigate the effects of preparation and metal loading on the adsorption stoichiometries of H_2 and CO on cobalt, (b) measure the reversible and irreversible H_2 and CO uptake, (c) determine the extent of reduction to the metallic state using magnetic measurements, and (d) calculate the average crystallite diameters of cobalt using the results from magnetic measurements and H_2 and CO chemisorption.

The hydrogen adsorption isotherms for the 9.0 wt% cobalt catalyst prepared by decomposition of $C_5H_5Co(CO)_2$ are shown in Figure 1. The isotherms are taken at 100°C and 200°C. Despite their slope, the total hydrogen uptakes at zero pressure for 100°C and 200°C are approximately the same (isotherms A). The second set of isotherms (isotherms B) are taken following the first set by pumping the sample to 1×10^{-4} for 0.5 hr. There is considerably higher reversible H_2 uptake at 200°C than at 100°C. The results indicate that the H_2 adsorption on cobalt is partly reversible and that the reversible part is affected by the adsorption temperature. Furthermore, experiments showed nearly zero hydrogen uptake on ZSM-5 itself at 100°C. In view of the absence of H_2 uptake on the support, the average crystallite diameters are calculated based on total hydrogen uptakes. The results obtained are in fair agreement with the ones calculated from irreversible CO uptakes on samples where complications from subcarbonyl formation with cobalt do not exist.

The cobalt dispersion and average crystallite diameters were calculated in a manner similar to Bartholomew and Pannel (1980). The fraction of metal atoms exposed (or dispersed), $D = Co_s/Co_t$, where Co_s is the number of surface atoms, and Co_t is the total number of cobalt atoms in the metallic state, was determined assuming the adsorption stoichiometry of $H/Co_s = 1$ for H_2 chemisorption. In the case of CO chemisorption, bridge-bonded and linear-surface species can occur. The degree of dispersion (D) was calculated for adsorption stoichiometries $CO/Co_s = 1$ and 0.5, respectively, for the two cases mentioned above.

The degree of reduction obtained from magnetization measurements was used to calculate Co_t. X-ray diffraction studies on the reduced catalyst have shown the presence of hcp cobalt crystallites. Assuming the latter to consist of spherical particles of uniform diameter d, one can show that $d_{(nm)} = 73.8/\%D$ (Reuel and Bartholomew, 1983). The cobalt crystallite sizes calculated in the above manner are shown in Table 1.

The following trends are visible from the results:

1. The CO and H_2 uptakes increase with increasing cobalt loadings.

2. Total H_2 uptakes increase approximately linearly with loading in the range 2 wt% to 9 wt% cobalt on ZSM-5 impregnated with $C_5H_5Co(CO)_2$.

3. The $CO_{irr.}/H$ adsorption ratio decreases with increasing cobalt loading.

4. Catalysts prepared from metal nitrate solution with cobalt loading in the range of 2.7 wt% to 5.0 wt% have a large $CO_{irr.}/H$ ratio. This is especially evident for the sample with 2.5 wt% cobalt.

5. The degree of reduction decreases with increasing cobalt dispersion.

The increase in $CO_{irr.}/H$ with increasing cobalt dispersion results from a combination of an increase in the CO/Co_s adsorption stoichoimetry and a decrease in the H_2 uptake. The decrease in degree of reduction and H_2 uptake with increasing metal dispersion may result from metal-support interaction as seen by Chin and Hercules (1982) in Co/Al_2O_3 catalyst. The unreduced cobalt probably is in the form of a spinel and is not available for H_2 adsorption. Ansorge and Förster (1981), in a study of 6 wt% Co/SiO_2, assigned the infrared band at 1900 cm^{-1} to bridged CO, and bands in the region 2050-2100 cm^{-1} to linear CO species. It is highly probable that the distribution of subcarbonyl, linear, and bridged CO surface species contribute to the variation in the CO adsorption stoichiometry. The very high CO uptake relative to H_2 uptake in the case of the 2.7 wt% cobalt (aqueous solution-impregnated) sample apparently results from formation of surface subcarbonyls species on highly dispersed cobalt. Such observations have been made earlier for supported-nickel (Rochester and Terrell, 1977; Bartholomew et al., 1980) and rhodium (Yates and Murrell, 1979) catalysts. The calculation of cobalt crystallite size based on CO chemisorption in the case of 2.7 wt% Co-ZSM-5 (aqueous solution-impregnated) sample is therefore not meaningful. Subcarbonyl formation on CO chemisorption appears to also exist, albeit to a much lower extent, in the case of 5.0 wt% Co-ZSM-5 (aqueous-solution-impregnated) sample.

With the exception of the samples mentioned in the previous paragraph, the cobalt crystallite diameter calculated from H_2 chemisorption is in reasonably good agreement with that calculated from CO chemisorption provided $0.5 \leq CO/Co_s \leq 1.0$. One can hypothesize that in catalysts with relativey high dispersion of cobalt (d ~5 nm), linearly bonded CO species are predominant, whereas in the case of catalysts where d $\geq$ 9 nm bridge-bonded CO species are favored. In the physically admixed catalyst, the cobalt crystallite size (~40 nm) is much larger than in the others and both linearly bonded and bridge-bonded CO species appear to occur.

The total hydrogen uptakes versus cobalt concentrations for the catalysts prepared by the aqueous solution of cobalt nitrate and organometallic impregnations are plotted in Figure 2. The result indicates that the total hydrogen uptake is nearly linear with increasing metal loading in the range of 2 wt% to 9 wt% cobalt for the catalyst prepared using the organometallic, whereas, the H_2 uptake is suppressed in the case of 2.7 wt% cobalt loading for the catalyst impregnated with metal nitrate. This appears to have resulted from a partial ion exchange of the acidic proton sites by Co^{2+} in the nitrate-impregnated catalyst. The Co^{2+} cations in the zeolite can not be reduced to the metal in flowing H_2 at 350°C. Since the metallic form of cobalt and not Co^{2+} is responsible for chemisorption, the uptake of hydrogen is correspondingly diminished in catalysts containing a fraction of the cobalt in ion-exchanged form.

Ion exchange was investigated by infrared monitoring of chemisorbed pyridine on the Co/ZSM-5 catalysts. In the case of aqueous solution impregnation, earlier infrared studies had shown that approximately 1.4 wt% of the Co/ZSM-5 catalysts was in the form of an ion-exchanged Co^{2+} species (Stencel et al., 1983). The ZSM-5 used in those investigations had $SiO_2/Al_2O_3 = 22$. Such a Co^{2+} concentration in ZSM-5 meant that the Lewis acid sites associated with the Co^{2+} constituted nearly one fourth of the total acidity in the ZSM-5. In the present investigation, the infrared analysis of chemisorbed pyridine is not as straightforward for the organometallic-impregnated samples as for catalysts using the other impregnation methods. This statement is based on the infrared spectra of the organometallic-impregnated sample after pyridine chemisorption, as shown in Figure 3. These spectra depict the 1200 cm^{-1} to 2000 cm^{-1} region, which contains a number of bands useful for interpretive procedures. First, the three bands between 1400 cm^{-1} and 1600 cm^{-1}, labeled L, B+L, and B, are associated with vibrational modes of chemisorbed pyridine and provide information on Lewis acid sites (L) and Brönsted acid sites (B). Second, the intense band centered near 1640 cm^{-1} is a superposition of bands due to chemisorbed pyridine and to OH groups. Third, the band at 1850 cm^{-1} is an overtone-combination band of the alumino-silicate framework of the ZSM-5. The integrated intensity of this 1860 cm^{-1} band (within the diagonal lines) is approximately identical in the reduced or calcined catalyst, Figure 3a and Figure 3b, respectively. This suggests that although the sample is removed from the infrared spectrometer to perform reduction or calcination treatments, the same amount of ZSM-5 is sampled before and after such treatments. Hence, assuming that the strength of the acid sites has not been altered severely during H_2 reduction or O_2 calcination, the decreased Brönsted and Lewis band intensity in Figure 3a as compared to Figure 3b suggests that the pyridine monitors fewer acid sites in the H_2-reduced catalyst than in the O_2-calcined catalyst. Such a decrease may be the result of a hydrocarbon/

carbonaceous residue left on the catalyst during organometallic impregnation, indicated by the band at 1415 cm^{-1} in the H_2-reduced sample, which hinders pyridine diffusion into the channels of ZSM-5. A 450°C O_2 calcination evidently causes a "burn-off" of such a residue, allowing access of pyridine into the ZSM-5.

A 450°C O_2 calcination of Co/ZSM-5 will also cause a redistribution of the Bronsted and Lewis acidity in the ZSM-5 by dehydroxylation and creation of Lewis acid sites. Hence, the threefold increase in Lewis acidity in Figure 3b as compared to Figure 3a, versus only a 25% increase in Bronsted acidity, may be caused by a number of factors. These factors, besides the availability of the channels of the ZSM-5 to pyridine diffusion and creation of Lewis acidity by dehydroxylation, include the ion exchange of Co^{2+} for H^+. To calculate the amount of ion exchange, the formalism developed previously (Stencel et al., 1983) can be utilized employing the fact that ZSM-5 with SiO_2/Al_2O_3 = 32 has an intensity ratio of Bronsted-to-Lewis peaks of approximately 2.0 after calcination at 450°C (Table 2). This calculation and the assumption of two pyridine adsorbed per Co^{2+} give the number of Co^{2+} ions per unit cell of ZSM-5 of 0.53. This number constitutes about one tenth of the total number of acid sites in the ZSM-5. Thus, although ion exchange has occurred in the organometallic-impregnated ZSM-5, the extent of ion exchange is considerably less than in the solution-impregnated ZSM-5.

(b) Catalytic Conversion of Synthesis Gas:

The (CO + H_2) conversion is plotted versus concentration of cobalt in the catalyst (Figure 4) for each method of preparation. In the case of solution-impregnated catalysts, the conversion increases rather rapidly with cobalt concentration in the range of about 3% to 6% cobalt and somewhat slowly in the range of about 6% to 9% cobalt. It is almost constant for organometallic-impregnated catalysts in the range of 3% to 9% cobalt. The conversion is nearly linear with cobalt concentration for the physically admixed catalysts in the range of 1.6% to 9.2% cobalt.

The effects of preparation method on catalyst activity and selectivity are shown in Tables 3 and 4 for catalysts with approximately 9 wt% and 3 wt% cobalt, respectively. At the metal loading of about 9% cobalt, there is only a slight difference between the conversions exhibited by the metal-nitrate-impregnated and organometallic-impregnated catalysts. Both have higher CO and H_2 conversions than the physically admixed catalyst. The C_5^+ fraction of the hydrocarbon product for the catalyst prepared using the organometallic is higher than the catalysts prepared by other methods. The physically admixed catalysts provide a much higher fraction of aromatics in the liquid hydrocarbon product, and higher C_3 and C_4 saturates than the solution- and organometallic-impregnated catalysts. In all cases, nearly 90% of the liquid hydrocarbon product was in the gasoline-boiling range, as determined by simulated distillation.

A more pronounced difference between the three preparations can be seen in Table 4 when the cobalt concentration is about 3 wt%. The organometallic-impregnated catalyst has considerably higher CO and H_2 conversion, as well as much higher selectivity for the C_5^+ fraction. The fraction of aromatics in the liquid hydrocarbon product is low for the catalyst prepared by organometallic-impregnation, and this amount decreases with time on stream. The amount of liquid hydrocarbon product from the other two catalysts was not sufficient to perform an FIA analysis for aromatics. However, the amount of C_3H_8 and C_4H_{10} in the product bears a correlation to the fraction of aromatics in the liquid hydrocarbon product. As explained by Dejaive et al. (1980), 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. The amounts of C_4H_{10} in the gas phase for the physically admixed, metal-nitrate-impregnated, and organometallic-impregnated catalysts are 23.0 wt%, 18.8 wt%, and 6.5 wt%, respectively, which indicates that the fraction of aromatics in the liquid hydrocarbon product should also decrease in the same order for the three catalyst preparations.

The (H_2 + CO) conversion and selectivity versus time on stream for the catalyst with 3% cobalt (calcined and uncalcined) prepared from $C_5H_5Co(CO)_2$ decomposition are shown in Figure 5. For the first 0-24 hr period, the sample that was calcined at 450°C for 1 hr has lower conversion that the uncalcined one, possibly the result of lower metal dispersion in the calcined samples. The C_1 fraction is lower and the C_5^+ fraction higher in the product from the calcined sample than for the uncalcined sample. The fraction of aromatics in the liquid hydrocarbon product from the calcined catalyst is nearly twice that from the uncalcined catalyst. The amount of CO_2 in the product is also lower for the calcined catalyst than for the uncalcined one. The difference in conversion and selectivity of CO_2 remains nearly unchanged with time on stream, whereas the selectivity of C_1 and C_5^+ is almost the same after 5 days for the two catalysts.

The physically admixed and organometallic-impregnated catalysts (9 wt%) were examined to provide information on some aspects of catalyst deactivation during 16 days of the test (Figure 6). There is a decline in (H_2 + CO) conversion with time on stream, and this is more noticeable for the physically admixed catalyst. Deactivation may be caused by the carbonaceous surface layer that forms from the dissociation of CO on the cobalt surface and grows with time on stream. This inactive overlayer (graphitic in nature) reduces the sites available for CO dissociation, and therefore, the conversion declines. There is a significantly higher conversion and selectivity to the C_5^+ fraction for the organometallic-impregnated catalyst in comparison to the physically admixed catalyst, and this difference stays nearly constant during the test. This may be due to the higher cobalt dispersion in the catalyst prepared by the organometallic impregnation than in the physically admixed catalyst.

The fraction of aromatics in the liquid product decreases, and the fraction of olefins increases, with time on stream for all the catalysts. It is known that the acid sites in H-ZSM-5 are responsible for the formation of aromatics by the dehydrocyclization of C_6^+ olefins. Deactivation of these acid sites with time on stream results in a decrease in the aromatic fraction and an increase in the olefin fraction of the liquid hydrocarbon product. The results show that there is a good correlation between a decrease in the fraction of aromatics and an increase in the $C_3^=/C_3$ ratio. One may conclude that the conversion of the C_3 olefin, a primary FT product, is a major indicator of the cyclization and aromatization activity. The rate of deactivation of the zeolite function can possibly be reduced by using ZSM-5 samples of smaller crystallite size (<0.1 μ) than those used in the present study.

Conclusions

In the preparation of Co-ZSM-5 catalysts, the use of an organometallic as a cobalt precursor at a low metal loading (3 wt%) resulted in increased metal dispersion and (H_2 + CO) conversion, in comparison to catalysts prepared by nitrate impregnation or physical admixture. The amount of gasoline-range product formed in a 24-hr period was about 10 times higher than that produced by metal nitrate or physically admixed catalysts. Magnetization measurements show that the degree of reduction decreases with increasing metal dispersion, and at low metal loading, the organometallic-impregnated samples exhibit a higher degree of reduction to the metallic state than samples with the same metal loading prepared from cobalt nitrate solution. Chemisorption results indicate that the CO/H ratio increases with increasing cobalt dispersion. This ratio is higher for samples prepared from cobalt nitrate solution than for the samples prepared by organometallic impregnation or the physical admixture method. This has probably resulted from a combination of decreases in the H_2 uptake and increases in the CO/Co_s ratio. The low H_2 uptake is an indication, especially at low metal loading, of a closer interaction of cobalt with the ZSM-5. The higher CO/H values for the 3 wt% to 5 wt% catalyst prepared from metal nitrate solution compared to those prepared by organometallic impregnation or the physical admixture method might be the result of changes in surface structure, with increasing dispersion causing the formation of surface subcarbonyl species.

The infrared spectra of pyridine chemisorbed on reduced 3 wt% cobalt/ZSM-5 catalyst prepared by organometallic impregnation indicate that the intensity ratio of Bronsted-to-Lewis peaks is nearly the same as is observed from ZSM-5, and the intensities of both peaks increase upon oxidation. The increase in intensity is possibly due to removal of carbonaceous species either on the surface or adsorbed on the acid sites, allowing the penetration of pyridine into the pore structure of ZSM-5. The oxidative removal of the carbonaceous species upon calcination also explains the increase in the fraction of aromatics in liquid hydrocarbon products from synthesis gas conversion over the catalysts.

Disclaimer

Reference in this report 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.

Acknowledgment

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TABLE 1

Chemisorption Results on Cobalt/ZSM-5 Catalysts

Wt% Cobalt in Catalyst	Method of Preparation	Degree of Reduction (%)	Total H_2 uptake at 100°C (μmol/g)	Irreversible CO uptake at 25°C (μmol/g)	(CO/H)	d* (nm) total H_2	d† (nm) Irr. CO
1.9	Organometallic Impregnated	58	12.2	26.8	1.10	5.7	2.6 (5.2)
3.0	Organometallic Impregnated	50	20.6	48.2	1.17	4.6	2.1 (4.2)
9.0	Organometallic Impregnated	100	52.9	62.8	0.59	10.6	9.0 (18.0)
2.7	Aqueous Impregnated	12	2.4	63.6	~13.0	8.5	---
5.0	Aqeuous solution Impreg.	75	22.5	88.0	1.96	10.4	2.7 (5.4)
9.0	Aqueous solution Impreg.	78	35.4	75.9	1.07	12.4	5.8 (11.6)
9.2	Physically admixed	98	13.2	16.5	0.62	42.7	34.2 (65.4)

*Assuming $H/Co_s = 1.0$

†$CO/Co_s = 0.5$. Quantities in parentheses were calculated assuming $CO/Co_s = 1.0$.

TABLE 2

Co/ZSM-5 Catalysts Studied by Acquisition of Infrared Spectra of Chemisorbed Pyridine. The ratio I_B/I_L is the intensity of the Brönsted peak divided by that of the Lewis peak

Catalyst	Pretreatment	Brönsted Band (cm^{-1})	Lewis Band (cm^{-1})	I_B/I_L
ZSM-5	Calcined	1547	1454	2.0
5.1 Co/ZSM-5/AQ	Calcined	1548	1453	0.27
5.1 Co/ZSM-5/AQ	Reduced	1548	1450	0.24
3.0% Co/ZSM-5/Org.	Reduced	1548	1450	1.87
3.0% Co/ZSM-5/Org.	Calcined	1549	1450	0.70

TABLE 3

Microreactor Results on Conversion and
Product Distribution from Co/ZSM-5 Catalysts.
$H_2/CO = 1$, $P = 21$ atm, $T = 280^{\circ}C$, $WHSV = 0.77$
(0-24 hour period)

	9.0% Co/ZSM-5 (organometallic impregnation)	9.0% Co/ZSM-5 (metal nitrate impregnation)	9.2% Co/ZSM-5 (physical mixture)
Cobalt crystallite size (nm)	10	12	43
CO Conversion (%)	53.5	56.5	47.5
H_2 Conversion (%)	86.5	85.9	78.0
Product Composition (wt%)			
CO_2	10.1	18.6	8.5
H_2O	53.7	46.1	53.8
CH_n	36.3	35.2	37.7
Composition of CH_n (wt%)			
CH_4	17.7	24.5	26.5
C_2H_4	0.0	0.0	0.0
C_2H_6	2.0	2.7	1.6
C_3H_6	1.2	0.8	0.0
C_3H_8	1.8	2.7	6.1
C_4H_8	1.0	0.7	0.6
C_4H_{10}	2.0	5.4	13.8
C_{5+}	74.3	63.1	51.4
Liquid Product Composition (vol%)			
Aromatics	13.5	22.0	50.5
Olefins	63.5	31.0	6.5
Saturates	23.0	47.0	43.0

TABLE 4

Microreactor Results on Conversion and Product Distribution from Co/ZSM-5 Catalysts.*
$H_2/CO = 1$, P = 21 atm, T = 280°C, WHSV = 0.77
(0-24 hour period)

	3.0% Co/ZSM-5 (organometallic impregnation)	2.7% Co/ZSM-5 (metal nitrate impregnation)	2.8% Co/ZSM-5 (physical mixture)
Cobalt crystallite size (nm)	5	8	—
CO Conversion (%)	52.9	21.0	24.8
H_2 Conversion (%)	85.2	34.3	46.0
Product Composition (wt%)			
CO_2	11.7	8.1	10.4
H_2O	52.5	56.6	53.7
CH_n	35.9	35.3	35.9
Composition of CH_n (wt%)			
CH_4	23.5	33.5	32.5
C_2H_4	0.0	0.0	0.0
C_2H_6	2.7	5.2	3.4
C_3H_6	0.0	0.0	0.0
C_3H_8	4.0	7.7	12.5
C_4H_8	1.2	0.9	0.0
C_4H_{10}	6.5	18.8	23.0
C_{5+}	62.1	33.9	28.6
Liquid Product Composition (vol%)			
Aromatics	13.0 (7.5)**	—	—
Olefins	44.5 (59.5)	—	—
Saturates	42.5 (33.0)	—	—

*Calcined at 450°C for 1 hour.

**The values in parentheses refer to the test on a catalyst that has not been calcined.

Figure Captions

Figure 1.

Hydrogen adsorption isotherms (O and O) at 100°C and (Δ and Δ) at 200°C on 9.0% Co ZSM-5 catalysts prepared by impregnation with $C_5H_5Co(CO)_2$. The isotherms A represent the total uptake, and the isotherms B the reversible uptake.

Figure 2.

Total H_2 uptake versus metal loadings for catalysts prepared by organometallic and cobalt nitrate solution impregnation.

Figure 3.

Infrared spectra of chemisorbed pyridine on 3.0% Co/ZSM-5; organometallic impregnation.

Figure 4.

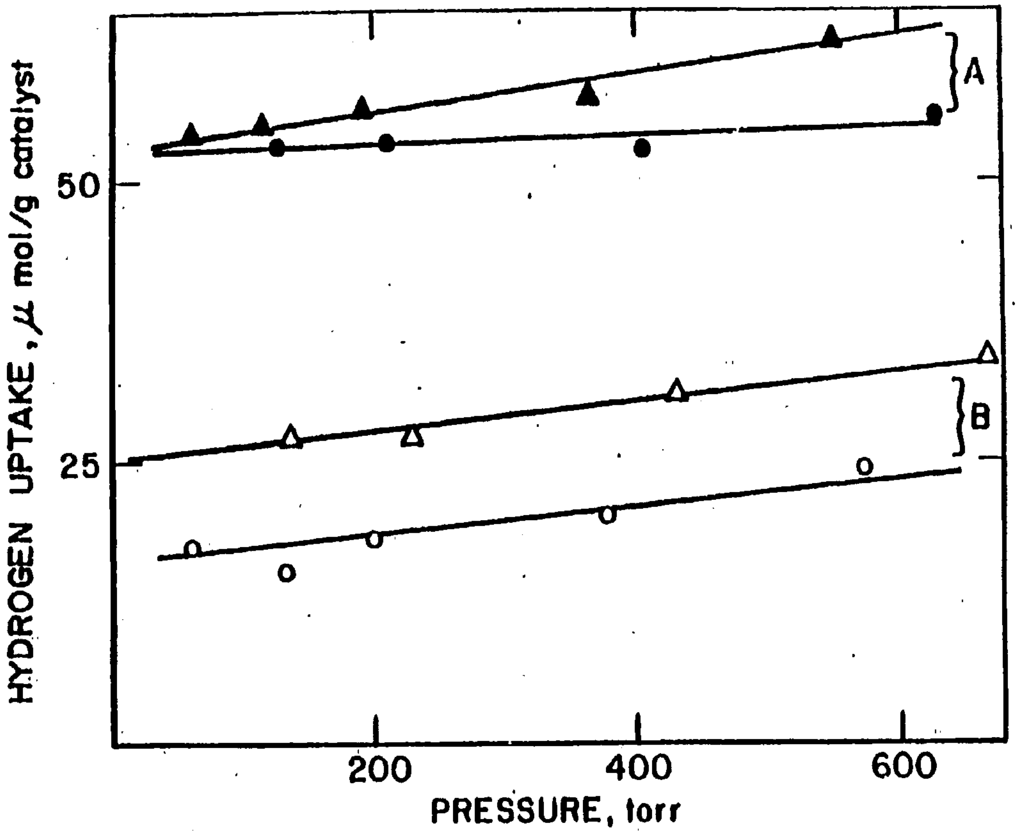
Catalytic activity versus the weight percent cobalt for the series of Co/ZSM-5 catalysts.

Figure 5.

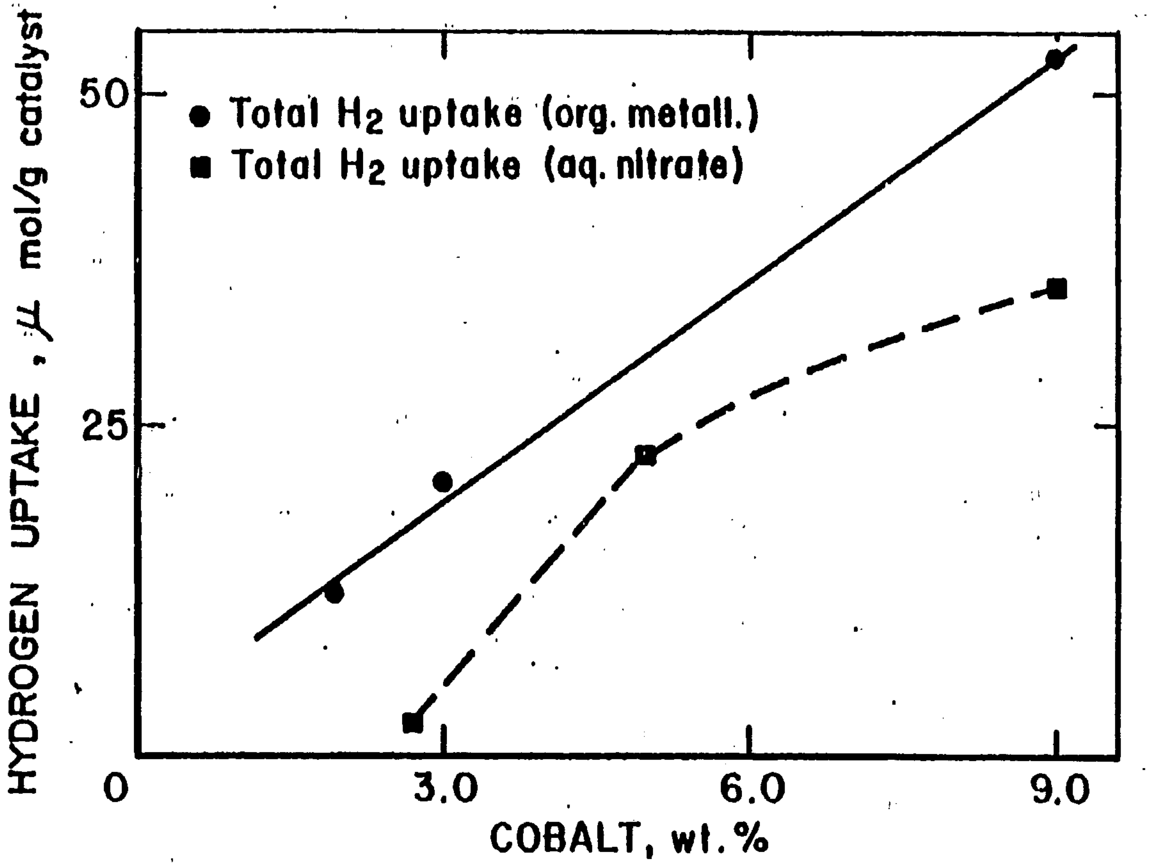
Catalytic activity and selectivity versus time on stream for the 3.0% Co/ZSM-5 catalysts prepared by impregnation with $C_5H_5Co(CO)_2$, (——) as prepared, (---) calcined at 450°C for 1 hr.

Figure 6.

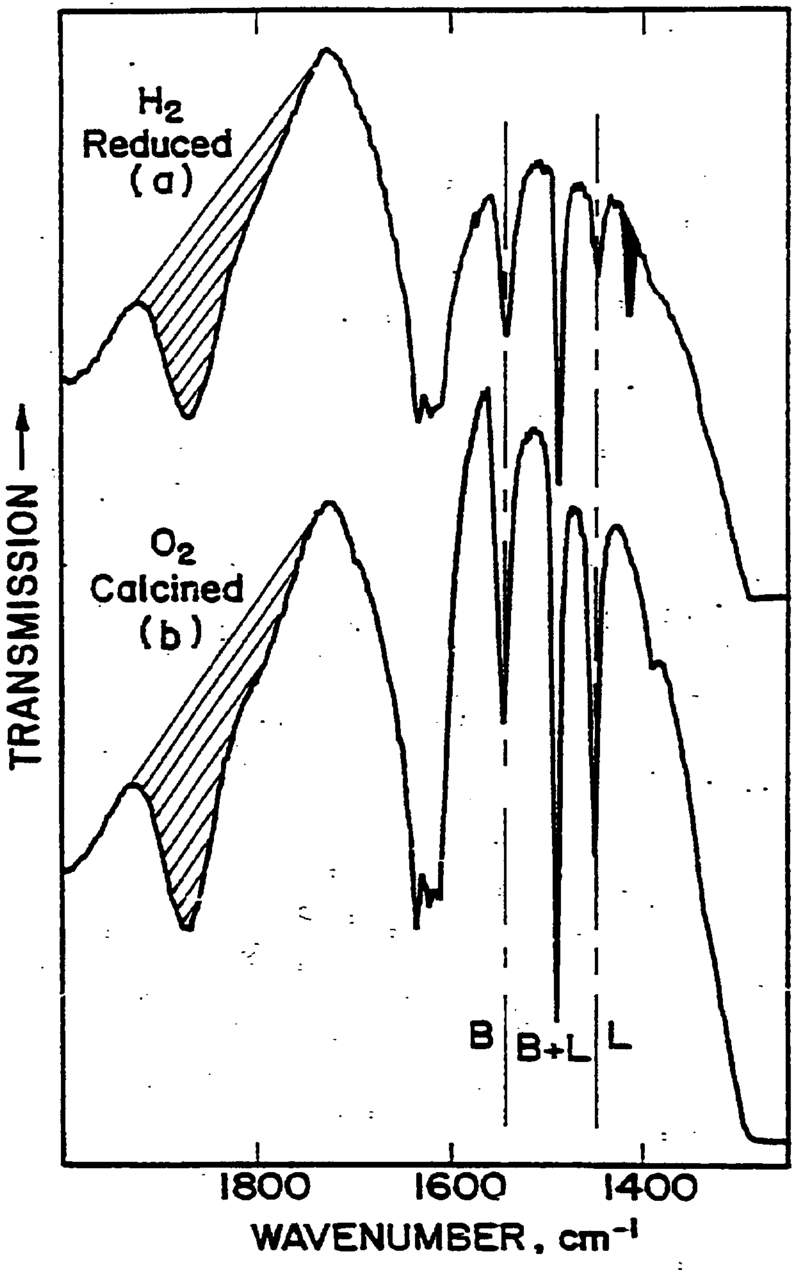
Catalytic activity and selectivity versus time on stream for (a) 9.0% Co/ZSM-5 prepared by organometallic-impregnation and (b) 9.2% Co/ZSM-5 physically admixed catalysts.


HYDROGEN UPTAKE, μ mol/g catalyst
50
25
PRESSURE, torr
200
400
600
A
B

BSI/4050

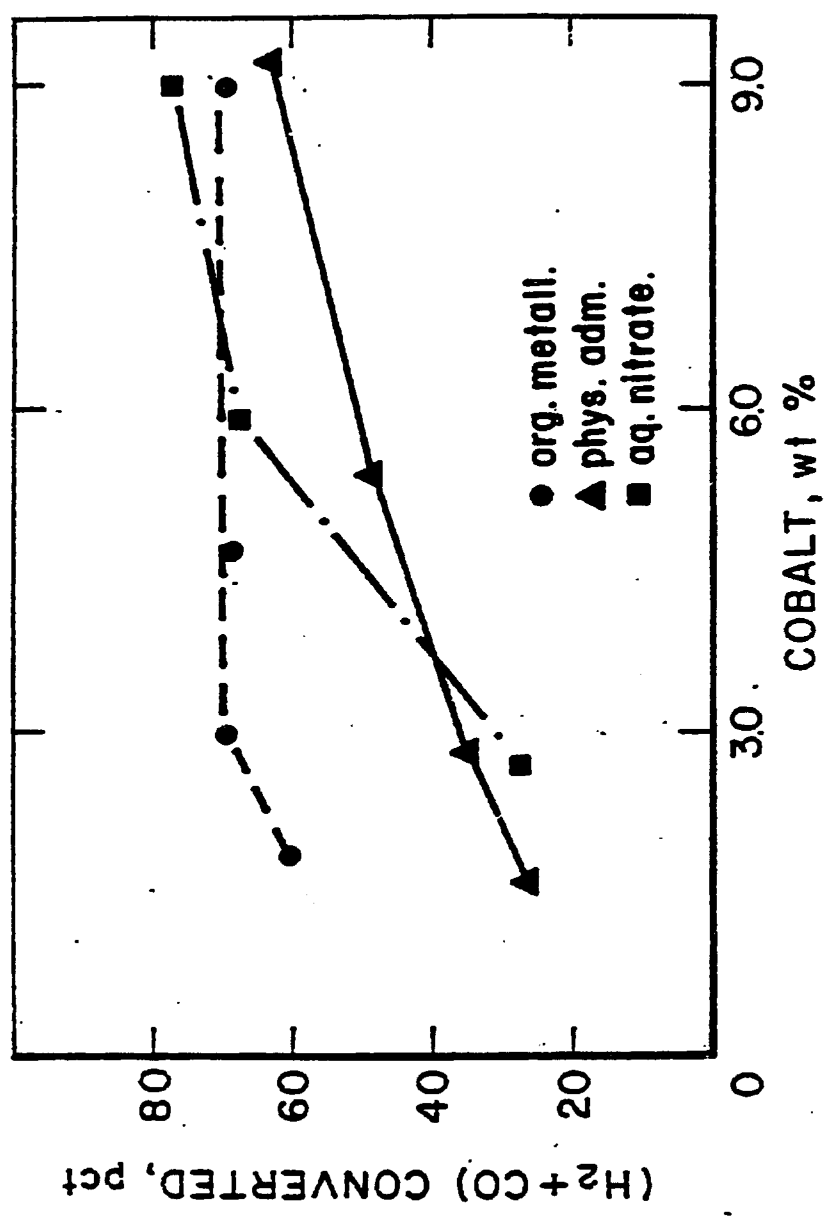

● Total H_2 uptake (org. metall.)
■ Total H_2 uptake (aq. nitrate)
HYDROGEN UPTAKE , μ mol/g catalyst
50
25
0
3.0
6.0
9.0
COBALT, wt.%

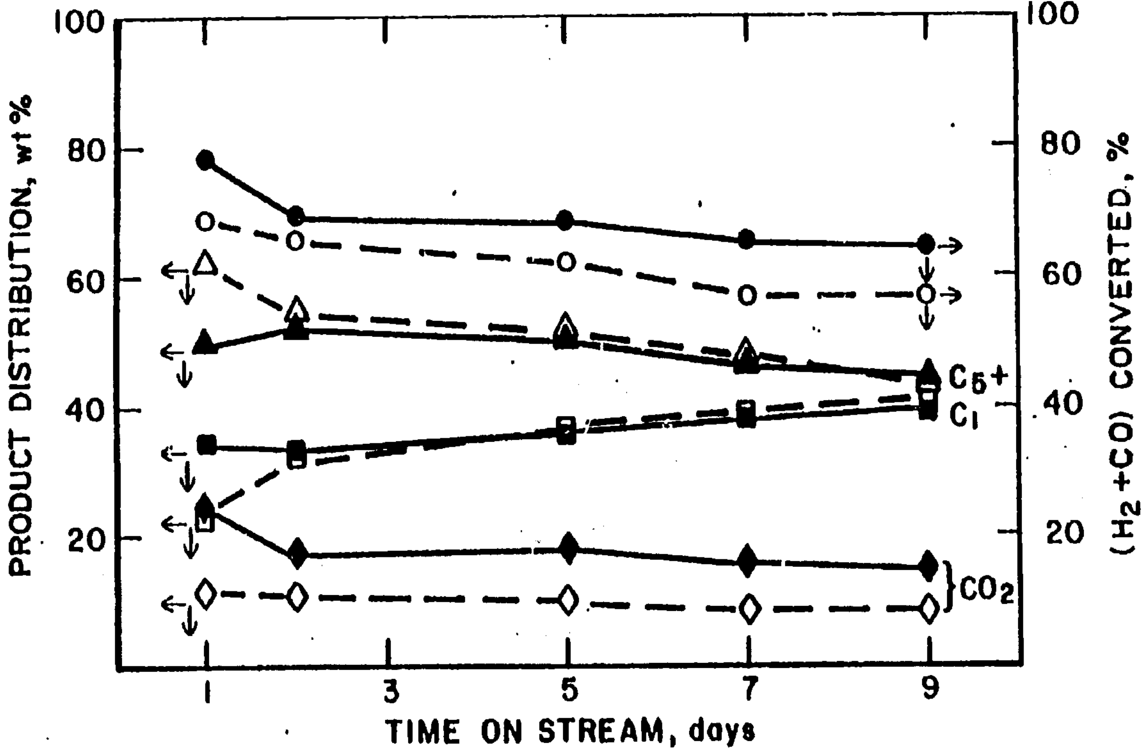
BSI/3793


H$_2$
Reduced
(a)
O$_2$
Calcined
(b)
TRANSMISSION
B
B+L
L
1800
1600
1400
WAVENUMBER, cm^{-1}

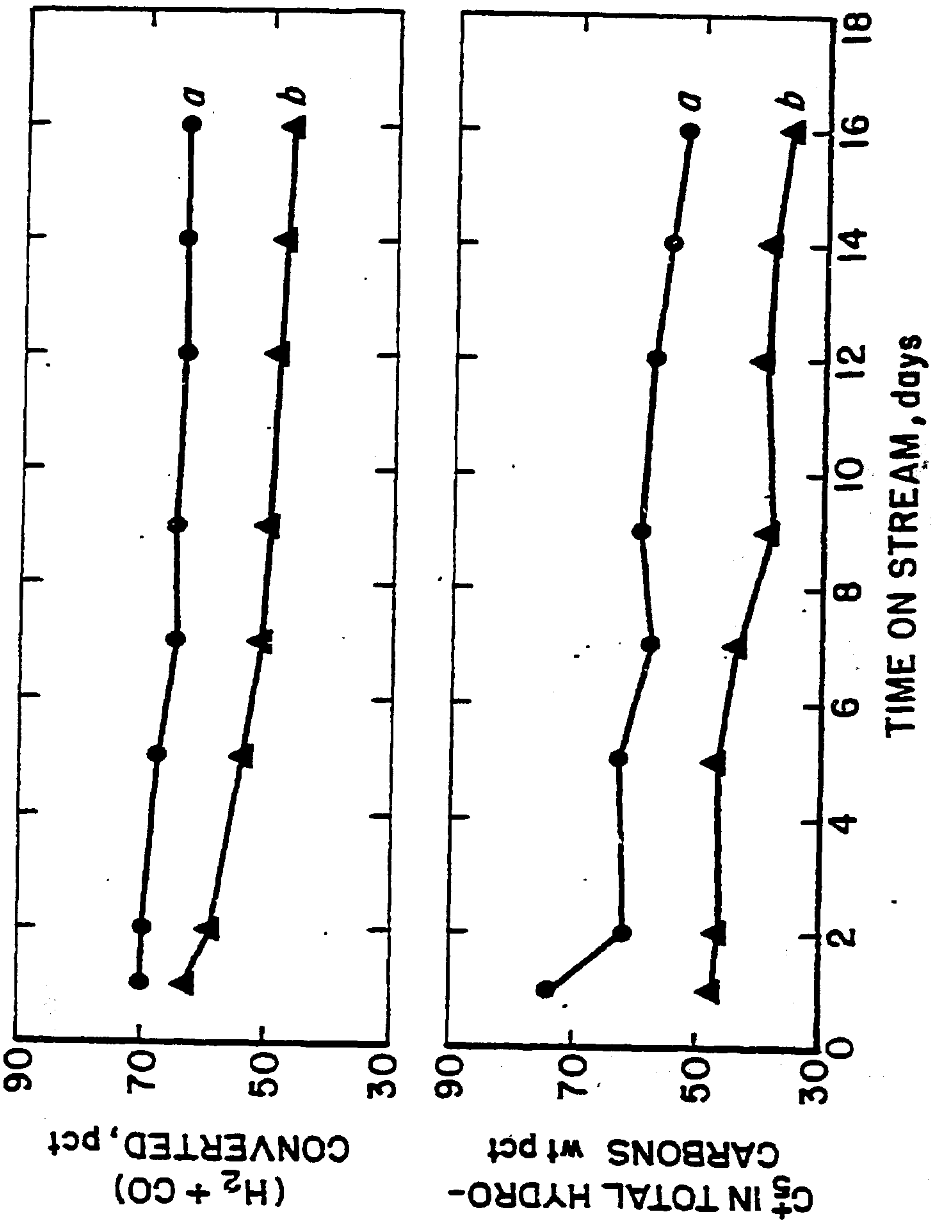
BSI/3897

BSI/3784


(H$_2$+CO) CONVERTED, pct
80
60
40
20
0
3.0
6.0
9.0
COBALT, wt %
● org. metall.
▲ phys. adm.
■ aq. nitrate.


100
80
60
40
20
PRODUCT DISTRIBUTION, wt %
100
80
60
40
20
(H₂ +CO) CONVERTED, %
C5+
C1
CO2
1
3
5
7
9
TIME ON STREAM, days

BSI/4051


(H$_2$ + CO) CONVERTED, pct
C_5^+ IN TOTAL HYDROCARBONS wt pct
TIME ON STREAM, days
90
70
50
30
0
2
4
6
8
10
12
14
16
18
a
b

BSI/1924

PROMOTION AND CHARACTERIZATION OF ZEOLITIC CATALYSTS USED IN THE SYNTHESIS OF HYDROCARBONS FROM SYNGAS

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Summary

Bifunctional metal-zeolite catalysts cobalt-ZSM-5 and cobalt-thoria-ZSM-5 were examined for the conversion of synthesis gas ($H_2/CO = 1$) at 280°C, 21 atm, and WHSV = 0.77 g/g cat. hr. The thoria in amounts as low as 0.4 wt% added to a cobalt-ZSM-5 with 9.0 wt% cobalt caused a considerable increase in synthesis gas conversion and selectivity to gasoline-range hydrocarbons. Some Co-ThO_2-ZSM-5 catalysts provided nearly 65 wt% selectivity to gasoline-range product that contained 26 vol% aromatics (alkylbenzenes). The selectivity to gasoline-range product exceeded the limit (48 wt%) set by Schulz-Flory kinetics. Chemisorption and magnetization studies were performed to determine metal particle size. Addition of thoria resulted in the decrease of the cobalt particle diameter from about 40 nm to 10 nm and caused an increase in CO/H adsorbed. The action of thoria as a promoter is possibly related to the presence of basic sites on its surface.

Introduction

The catalytic conversion of synthesis gas (CO + H_2) over group VIII metals leads to the formation of hydrocarbons and oxygenates by the Fischer-Tropsch (F-T) synthesis reaction (1). The formation of these products appears to take place by the addition of a single carbon intermediate to a growing chain. If the chain growth probability is independent of chain length, the product distribution is governed by the Schulz-Flory (S-F) polymerization kinetics (1); the maximum selectivity that could then be obtained for the gasoline fraction (C_5-C_{11}) is 48 percent by weight of the total hydrocarbons formed. It is well known that olefinic and oxygenated products from F-T synthesis can be converted over the medium-pore acidic zeolite H-ZSM-5 to gasoline-range hydrocarbons containing aromatics. In this manner, the F-T products can be upgraded to yield high octane components. The method offers a possibility to circumvent S-F kinetics and obtain a gasoline-range product in excess of 48 percent of the total hydrocarbon product.

Metal-zeolite catalysts made by combining an F-T component with ZSM-5 have been examined in the conversion of synthesis gas (2-5). Such catalysts can provide a liquid hydrocarbon product of the high octane gasoline type directly from synthesis gas. The continuing efforts at this Center have been toward understanding the influence of the method of catalyst preparation on the conversion and selectivity.

A recent investigation examined cobalt-ZSM-5 catalysts that were prepared by two different methods: (a) impregnation of ZSM-5 with cobalt nitrate solution and (b) physical admixture of precipitated cobalt with ZSM-5 (6). The selectivity to aromatics was higher with the catalysts prepared by the physical admixture method. The solution impregnation method resulted in some cobalt in ion-exchanged form (as Co^{2+}) — nearly 1.7 wt% of the catalyst. The ion-exchange resulted in a decrease in the number of Brønsted acid sites and an increase in the number of Lewis acid sites. The additional Lewis acid sites were not catalytically active. It was inferred that the decrease in the number of Brønsted acid sites in the catalysts prepared by the solution impregnation method resulted in a lower selectivity to aromatics.

The present investigation is concerned with attempts to increase the liquid hydrocarbon yield in synthesis gas conversion over cobalt-ZSM-5 catalysts. Early work had shown that the addition of thoria as a promoter to cobalt-kieselguhr resulted in an increased yield of C_{5+} hydrocarbons (7). It was of interest to examine the promotional effect of thoria on cobalt-ZSM-5 catalysts. In this paper, the results of experiments on synthesis gas conversion over cobalt-ZSM-5 and cobalt-thoria-ZSM-5 are reported. The physical admixture method of preparing the catalyst was used, since this method had little effect on the Brønsted acid sites of the zeolite. The CO and H_2 chemisorption studies were conducted to examine the possible influence of thoria on the metal surface area. The degree of reduction of the cobalt in the catalysts after hydrogen treatment was determined by magnetization studies.

Experimental

Preparation of Catalysts. The ZSM-5, with $SiO_2/Al_2O_3 \sim 30$, was synthesized using the procedure given in the patent literature by Argauer and Landolt (8) with minor modifications. The zeolite was calcined in air at 538°C to decompose the TPA^+ cation. It was converted to the ammonium form by three successive exchanges using NH_4Cl solution. It was then calcined in air at 538°C to obtain the H-form.

The F-T component (cobalt or cobalt-thoria) was initially made as a precipitate by adding a 10 wt% sodium carbonate solution at 70°C to a second solution also at 70°C containing 10 wt% cobalt nitrate and the required amount of thorium nitrate until a pH of 7 was reached. The precipitate was filtered, washed with water thoroughly to ensure a content of less than 0.1 wt% Na, and dried at 110°C. The dry metal oxide and the dry zeolite were each sieved to -200 mesh, then thoroughly mixed and formed into 3-mm-diameter pellets.

Syngas Conversion Tests. A 1.35-g catalyst sample was introduced into a vertical, down-flow reactor tube of 1-cm inner diameter. The bed height of the catalyst was 2.5 cm. The catalyst was heated in flowing nitrogen at 21 bar to 450°C and kept at that temperature for 16 hours. The temperature was lowered to 190°C, and hydrogen at 21 bar and a flow rate of 70 mL/min was introduced. The temperature of the catalyst was raised to 350°C at the rate of 2°C/min, and the catalyst was kept at that temperature for 16 hours. The temperature was lowered to 250°C; and the pressure, to 7 bar. Syngas with the composition $H_2/CO = 1$ was introduced and the pressure was slowly raised to 21 bar. The temperature was raised to 280°C, and a flow of 0.77 g/g cat. hr was maintained.

The products of the reaction were mainly CO_2, H_2O, and hydrocarbons. A hot trap at 175°C, following the reactor, collected wax and heavy oil. A cold trap at 0^{o}C, following the hot trap, collected water, gasoline-range products, and light oil. The remaining product that was not in the condensed phase and the unconverted feed gas moved past the back pressure regulator. Samples of the exiting gas were collected periodically and analyzed for H_2, CO, CO_2, and C_1-C_7 hydrocarbons using a gas chromatograph. The liquid product collected in the cold trap was separated physically into aqueous and hydrocarbon fractions. It is assumed that the liquid hydrocarbon product consists of C_5+. Material recovery, as shown by the mass balance procedure, was usually better than 96%. The amount of product collected in the hot trap, if any, was very small in comparison to that collected in the cold trap. The hydrocarbon product from the latter 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). The results of such separation are included in Tables I and II. The combined aromatic and paraffin fractions were analyzed by ASTM-D-2789 mass spectrometry to find the percentage of cycloparaffins, and the distribution of the alkylbenzenes by carbon number up to C_{12}.

Chemisorption Measurements. Hydrogen and carbon monoxide adsorption measurements were performed using a conventional glass volumetric adsorption apparatus. The sample was reduced at 350^{o}C for 16 hours. The H_2 adsorption measurements were conducted at 100^{o}C. Adsorption isotherms such as those shown in Figure 1 were obtained.

The CO adsorption measurements were performed at 25^{o}C. The first adsorption isotherm that was taken (Figure 2) represented the total CO uptake.

The sample chamber was pumped out to 10^{-3} torr for 0.5 hr. The second isotherm was taken (Figure 2), and it represented the reversible part of the CO uptake. The difference between the uptakes in the two isotherms representing the irreversible uptake was considered to be the CO chemisorbed on the metallic cobalt, in accordance with previous investigations (9).

Samples for magnetic analysis were placed in 4-mm-o.d. glass tubes and reduced in flowing H_2 at 350°C for 16 hours. The tubes were then sealed under vacuum. The magnetic measurements were performed using a vibrating sample magnetometer in applied fields up to 15 kOe. The magnetization values obtained were compared with the known magnetization of bulk cobalt, and the degree of reduction was obtained.

Results and Discussion

Catalytic Conversion of Synthesis Gas. The experiments were conducted to provide information on the influence of cobalt and thoria concentrations on the conversion and selectivity of the catalysts. Initially, experiments were performed with catalysts containing cobalt in the range 2.8 to 10.7 wt%. Thoria was added to some catalysts, the ratio of thoria to cobalt being about 0.16. The changes in conversion and C_5+ selectivity with cobalt loading are shown in Figure 3.

The CO + H_2 conversion and C_5+ yield are much higher, and the methane yield is lower, for Co-ThO_2-ZSM-5 catalysts than for Co-ZSM-5 catalysts. The conversion and C_5+ yield increase markedly with cobalt content for Co-ZSM-5 catalysts, whereas they are relatively insensitive to cobalt concentration for Co-ThO_2-ZSM-5 catalysts.

In another set of experiments, the influence of promoter concentration on the conversion and selectivity of the catalysts was examined. The cobalt concentration was maintained nearly constant at 9.0 wt%, and the concentration of thoria was changed from 0.0 to 1.5 wt%. Chemisorption of CO and H_2 was performed on the same catalysts in an effort to relate catalytic activity to possible changes in metal particle size upon promoter addition. The results of the catalytic activity tests for the first 24-hour period are shown in Table I.

The olefinic product is very small with Co-ZSM-5 catalysts, indicating very efficient secondary conversion to aromatics over the H-ZSM-5 component. In all cases, nearly 90% of the liquid hydrocarbon product was in the gasoline boiling range as determined by simulated distillation.

It is remarkable that even a small amount of promoter, as low as 0.4 wt% ThO_2, causes significant increase in conversion, shift activity, and C_5+ selectivity. There is decrease in methane formation and in the fraction of aromatics in the liquid hydrocarbon product. Increase in ThO_2 concentration beyond 0.8 wt% does not result in further significant changes in conversion or selectivity.

To understand the role of thoria as a promoter, it is important to examine the selectivities of catalysts that show comparable CO and H_2 conversions. In Table II, the conversion and product distribution from a catalyst containing

10.3 wt% cobalt and no thoria is compared with those from a catalyst containing 2.9 wt% cobalt and 0.5 wt% thoria. At comparable CO and H_2 conversions, it is seen that the catalyst containing thoria provides lower methane yield, higher C_5+ fraction and a lower fraction of aromatics than the catalyst that does not contain thoria.

The Co-ThO_2-ZSM-5 catalysts provided nearly 65 wt% of the hydrocarbon product in the gasoline boiling range during the initial 24-hour period, thus exceeding the amount predicted (48%) by Schulz-Flory polymerization kinetics (1). The NMR studies showed a high degree of branching of the olefin and saturate fractions in the liquid product obtained from such catalysts. In combination with the aromatic fraction, which is nearly 20 vol%, the liquid hydrocarbon product is of the high octane gasoline type.

X-ray photoelectron spectroscopy studies on a hydrogen-treated Co-ThO_2-ZSM-5 sample showed that cobalt was present predominantly in the metallic form, but thorium remained in the Th^{4+} state, i.e., possibly as ThO_2 (10). There is a strong indication, as will be discussed later, that the promoter action arises from an interaction between metallic cobalt particles and thoria.

Chemisorption of CO and H_2 Chemisorption studies were performed on three of the catalysts that were shown in Table I. The results of chemisorption measurements are shown in Table III. The degree of reduction in flowing H_2 at 350°C after 16 hours was obtained from magnetization studies.

The hydrogen uptake was measured at 100°C, since recent work has shown that maximum adsorption on unsupported cobalt occurred at this temperature (11). The hydrogen adsorption isotherms for the two catalysts containing, respectively, 0.0 and 1.5 wt% ThO_2 are indicated in Figure 1.

The values of hydrogen uptake were extrapolated to zero hydrogen pressure from the high pressure linear portion of the isotherm as outlined for nickel catalysts by other workers (9, 12). The extrapolated values are reported in Table III. The considerable increase in hydrogen uptake upon promoter addition is noteworthy.

The CO adsorption isotherms on Co-ZSM-5 containing 9.2 wt% cobalt and on Co-ThO_2-ZSM-5 containing 8.9 wt% cobalt and 1.5 wt% thoria are shown in Figure 2. The addition of thoria to the cobalt-ZSM-5 catalyst has resulted in a sizable increase in the irreversible uptake of CO. The irreversible CO uptake extrapolated to zero CO pressure is given in Table III.

The metal dispersions $D = Co_s/Co_t$, where Co_s is the number of surface cobalt atoms and Co_t is the total number of cobalt atoms, were calculated assuming adsorption stoichiometries of $H/Co_s = 1.0$ for H_2 chemisorption, and $CO/Co_s = 0.5$ for CO chemisorption. These stoichiometries are obeyed approximately by unsupported cobalt according to recent work (13). Average crystallite diameters were calculated from %D assuming spherical hcp metal crystallites of uniform diameter d. Then d (in nm) = 73.81/%D.

The average diameters calculated in the above manner are shown in Table III. It is possible that CO is chemisorbed partly in linear form (CO/Co_S = 1.0) and partly in bridge-bonded form (CO/Co_S = 0.5). The relative amounts of the two forms appear to be dependent on the thoria concentration. An examination of CO/H values in Table III, suggests that CO is predominantly in the bridge-bonded form in the absence of thoria. The addition of thoria increases the CO/H value which is nearly unity in the catalyst with 1.5 wt% thoria, suggesting the linear form of chemisorbed CO.

The addition of thoria to Co-ZSM-5 resulted in a considerable reduction in cobalt particle diameter, i.e., increase in cobalt surface area (see Table III). Thoria has been regarded as a structural promoter (7), resisting the sintering of the cobalt particles during reduction. The present studies tend to support this possibility as one of the influences of thoria. The increase in surface area may be responsible for the enhanced conversion of CO and H_2 upon the addition of thoria to the catalyst (Table I and Figure 3).

Effect of Promoter on Selectivity. In addition to the increase in conversion upon ThO_2 incorporation in Co-ZSM-5, there are interesting effects on selectivity (Table I). The methane yield is reduced and the yield of C_{5+} is increased. The effect is reminiscent of the influence of potassium promotion on the selectivity of iron Fischer-Tropsch catalysts (14).

The CO adsorption results in a net withdrawal of electrons from the metal, whereas hydrogen adsorption tends to donate electrons to the metal. Since ThO_2 possesses basic surface sites (15), it can be expected to donate electrons to the metal. The presence of thoria would enhance the adsorption of CO, while weakening that of H_2. The increase in CO/H adsorbed when thoria is added to the catalyst (Table III) supports the conjecture. This leads to decreased hydrogenation of surface species. Chain termination and desorption are facilitated by hydrogenation. The influence of thoria is to encourage chain growth and yield products with higher molecular weight. The product is more olefinic owing to the reduction in hydrogenation ability.

Concluding Remarks

The experiments show the marked influence of thoria in increasing the conversion and liquid hydrocarbon selectivity of cobalt-ZSM-5 catalysts in synthesis gas reaction. Chemisorption and magnetization measurements have been useful in showing that one of the effects of thoria addition has been to increase the dispersion of metallic cobalt. The increase in CO/H adsorbed with thoria addition may be connected with the selectivity shift to heavier products. The aromatic concentration in the liquid product is sufficiently high (~ 20 vol%) in the initial 24-hour period to provide high octane gasoline.

Using cobalt-thoria-ZSM-5 catalysts for synthesis gas conversion, it is possible to obtain nearly 65 wt% of the hydrocarbon product in the gasoline boiling range. The selectivity to gasoline exceeds the limit of 48 wt% set by Schulz-Flory kinetics. Some of the primary F-T products, such as C_2-C_4 olefins and oxygenates, are converted to gasoline-range components, including aromatics, by the catalytic action and shape-selective function of ZSM-5. The heavier hydrocarbons (C_{11+}) that are formed in the F-T reactions are cracked by ZSM-5 to provide additional gasoline-range product.

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TABLE I. Influence of Promoter (ThO_2) Addition on the Activity and Selectivity of Co-ZSM-5 Catalysts.
SiO_2/Al_2O_3 in H-ZSM-5 $\sim$ 39

Test Conditions: $H_2/CO \sim 1$, P = 21 bar, T = 280°C
Feed Rate = 0.77 g/g cat. hr.

Co in Catalyst (wt%)	9.2	8.8	8.5	8.9
ThO_2 in Catalyst (wt%)	0.0	0.4	0.8	1.5
CO Conversion (%)	47.5	67.1	71.1	74.0
H_2 Conversion (%)	78.0	88.1	89.0	91.6
$CO+H_2$ Conversion (%)	63.2	77.9	80.3	83.1
Product Composition (wt%)				
CO_2	8.5	27.0	26.5	27.6
H_2O	53.8	39.8	40.3	37.9
CH_n	37.7	27.0	26.4	34.4
Composition of CH_n (wt%)				
CH_4	26.5	19.4	16.1	16.4
C_2H_4	0.0	0.0	0.1	0.1
C_2H_6	1.6	2.6	2.0	0.1
C_3H_6	0.0	0.0	0.2	0.3
C_3H_8	6.1	3.9	3.4	2.9
C_4H_8	0.6	0.9	0.8	0.7
C_4H_{10}	13.8	6.0	6.1	5.4
C_5+	51.4	67.2	71.4	72.5
Liquid Product Composition (vol%)				
Aromatics	50.5	18.5	21.5	20.0
Olefins	6.5	48.0	39.5	44.5
Saturates	43.0	33.5	39.0	35.5

TABLE II. The Product Distribution From Two Co-ZSM-5 Catalysts, One Promoted With Thoria and the Other With no Thoria, at Comparable CO and H_2 Conversions.

Test Conditions: $H_2/CO \sim 1$, P = 21 bar, T = 280°C
Feed Rate = 0.66 g/g cat. hr.

Co in Catalyst (wt%)	10.3	2.9
ThO_2 in Catalyst (wt%)	0.0	0.5
CO Conversion (%)	52.1	60.6
H_2 Conversion (%)	80.4	85.0
$CO+H_2$ Conversion (%)	66.3	72.8
<u>Product Composition (wt%)</u>		
CO_2	15.7	17.1
H_2O	52.4	48.1
CH_n	31.9	34.8
<u>Composition of CH_n (wt%)</u>		
CH_4	31.8	12.6
C_2H_4	0.0	0.0
C_2H_6	1.5	0.8
C_3H_6	0.0	0.0
C_3H_8	6.7	6.1
C_4H_8	0.0	0.0
C_4H_{10}	11.2	13.5
C_5+	48.7	67.3
<u>Liquid Product Composition (vol%)</u>		
Aromatics	64.0	34.0
Olefins	1.0	3.5
Saturates	35.0	62.5

TABLE III. Chemisorption Results on Co-ZSM-5 and Co-ThO_2-ZSM-5 Catalysts

Catalyst Composition (wt%)		Degree of Reduction (%)	Gas Uptake[a] (μmole g^{-1})		$\frac{CO}{Co}$	$\frac{H}{Co}$	$\frac{CO}{H}$	d^b (nm)	d^c (nm)	
Cobalt	Thoria		CO@25°C	H_2@100°C					(i)	(ii)
9.2	0.0	98	16.4	13.2	0.0107	0.0173	0.618	42.3	64.8	34.4
8.5	0.8	92	56.3	33.3	0.0424	0.0502	0.845	14.7	17.4	8.7
8.9	1.5	80	70.3	34.0	0.0581	0.0563	1.033	13.1	12.6	6.3

[a] Irreversible CO adsorption and total H_2 adsorption

[b] Based on total H_2 adsorption

[c] Based on irreversible CO adsorption, assuming (i) $CO/Co_s = 1.0$, and (ii) $CO/Co_s = 0.5$

Captions for Figures

Figure 1. Hydrogen adsorption isotherms for Co-ZSM-5 containing 9.2 wt% Co, and Co-ThO_2-ZSM-5 containing 8.9 wt% Co + 1.5 wt% ThO_2.

Figure 2. CO adsorption isotherms for Co-ZSM-5 containing 9.2 wt% Co, and Co-ThO_2-ZSM-5 containing 9.2 wt% Co and 8.9 wt% Co + 1.5 wt% ThO_2.

Figure 3. Variation of conversion and C_5+ selectivity with cobalt content for the Co-ZSM-5 and Co-ThO_2-ZSM-5 catalysts.

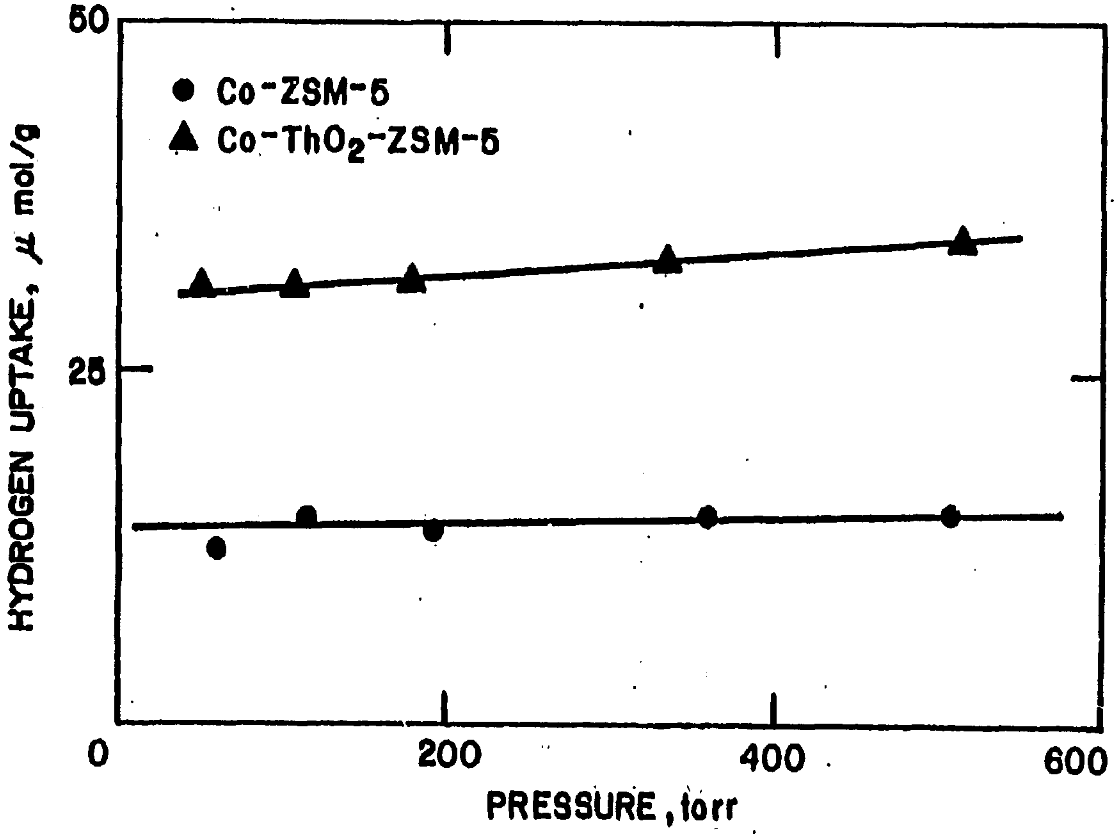
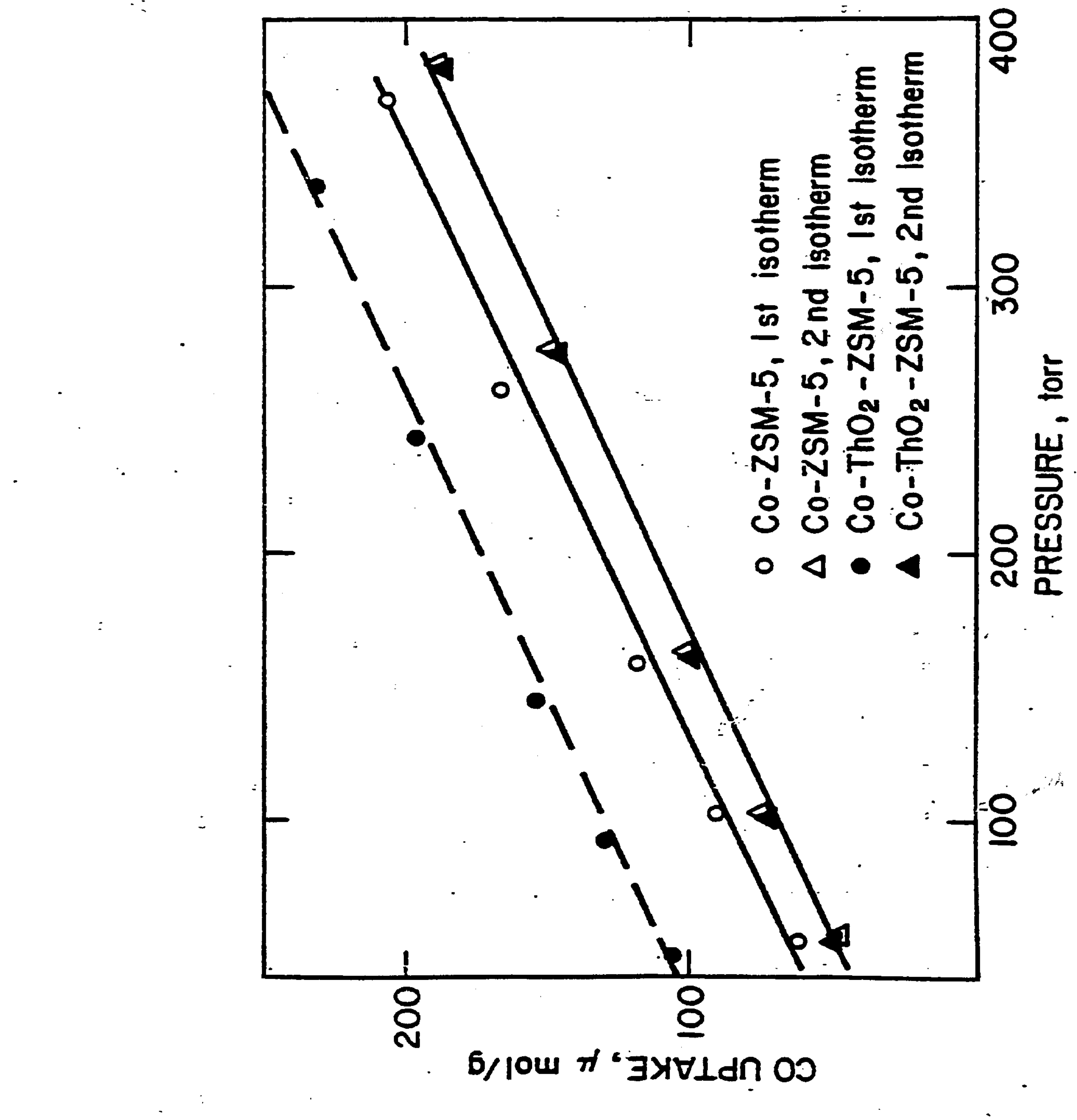

Co-ZSM-5
Co-ThO$_2$-ZSM-5
HYDROGEN UPTAKE, μ mol/g
50
25
0
200
400
600
PRESSURE, torr

Fig 1

CO UPTAKE, μ mol/g
200
100
PRESSURE, torr
100
200
300
400
○ Co-ZSM-5, 1st isotherm
△ Co-ZSM-5, 2nd isotherm
● Co-ThO$_2$-ZSM-5, 1st isotherm
▲ Co-ThO$_2$-ZSM-5, 2nd isotherm

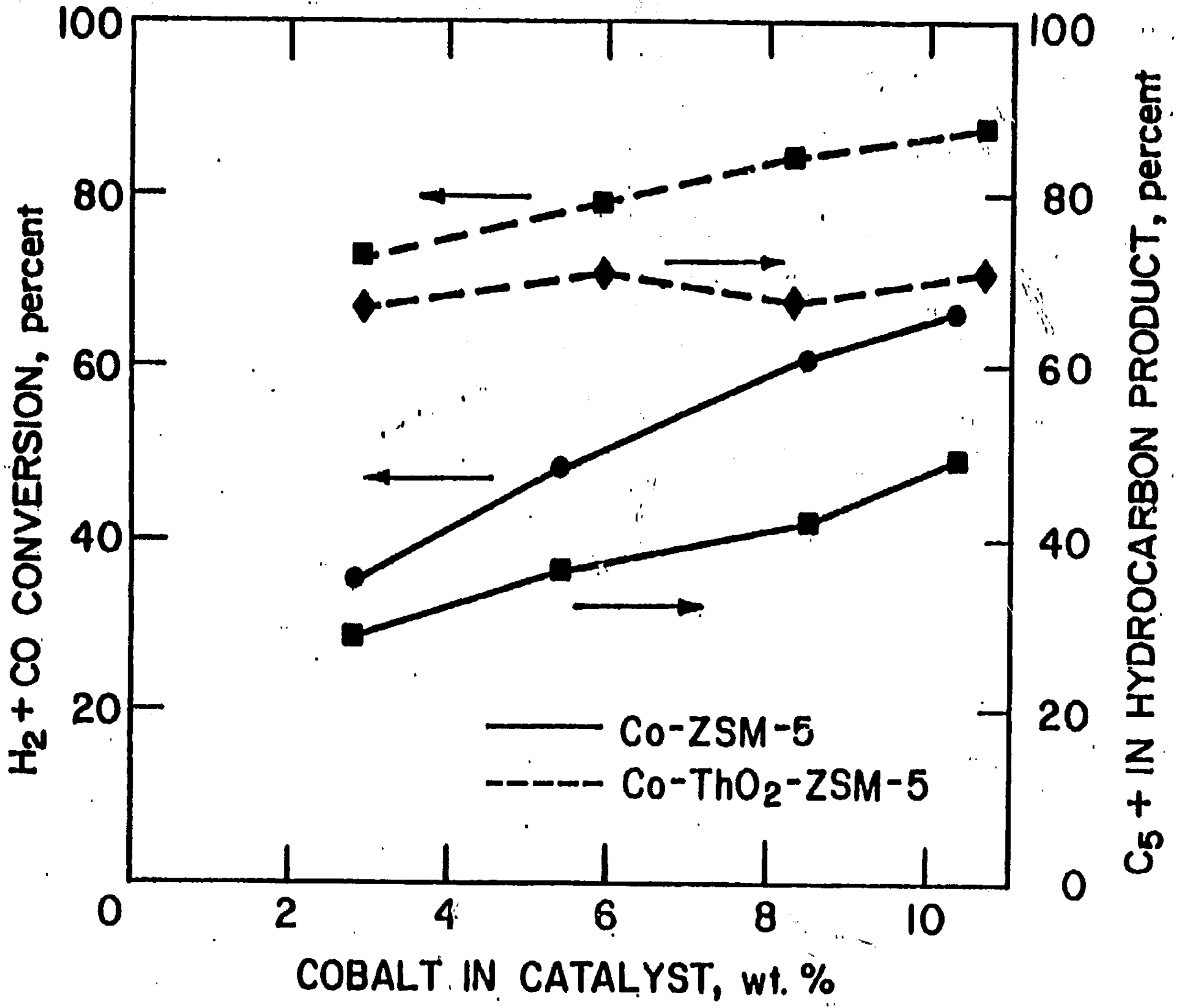

100
80
60
40
20
0
H$_2$ + CO CONVERSION, percent
2
4
6
8
10
COBALT IN CATALYST, wt. %
100
80
60
40
20
0
C$_5$ + IN HYDROCARBON PRODUCT, percent
Co-ZSM-5
Co-ThO$_2$-ZSM-5

Fig 3