

Metal Particle Characterization of Zeolite-Based Syngas Conversion Catalysts

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INTRODUCTION

The conversion of $\text{CO} + \text{H}_2$ in one step to a mixture of hydrocarbon species that are the constituents of high octane gasoline appears possible with catalysts composed of ZSM-5 and a group VIII metal (1-5). The group VIII metal acts as a Fischer-Tropsch (F-T) catalyst and converts synthesis gas to a mixture of olefins, paraffins, and oxygenates. The ZSM-5 component of the catalyst converts some of the F-T intermediates and products to aromatics and branched-hydrocarbon species.

The present study attempts to characterize the metal crystallite size and the degree of reduction of cobalt-ZSM-5 catalysts using chemisorption and magnetization measurements. The catalysts prepared by the solution-impregnation method were examined. It was realized that the method could result in partial ion exchange of the acidic protons in ZSM-5 with cobalt ions (5-7). The ion-exchanged cobalt (Co^{2+}) is catalytically inactive in synthesis gas conversion (6,7), since it cannot be reduced to metallic cobalt under usual reduction treatment, namely, flowing hydrogen at 350°C. The present study attempts to demonstrate how chemisorption and magnetization measurements on Co/ZSM-5 catalysts with different Co concentrations can enable one to estimate the weight percent Co that has been ion-exchanged into ZSM-5.

It has been reported (8,9) that $(\text{Fe}^{2+}, \text{NH}_4^+)Y$ can react with an anionic, metal-containing coordination compound that is water-soluble, such as $(\text{NH}_4)_3[\text{Fe}(\text{CN})_6]$, to yield an insoluble compound, $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$, distributed throughout the zeolite while the zeolite itself returns to the ammonium form. The insoluble complex can later be reduced in hydrogen to finely dispersed metal in the zeolite (9). The present work attempts to examine whether the above method could be used to convert ion-exchanged Co^{2+} in ZSM-5 to a reducible and catalytically active form. Since it was of interest to examine the catalytic activities of both the metal component and the zeolite component, before and after the reaction with the coordination compound, separate experiments were performed with syngas and ethylene as the reactants. Syngas conversion is primarily catalyzed by the metal component; and ethylene conversion, by the zeolite component in the catalyst.

EXPERIMENTAL

(a) Preparation of Catalysts

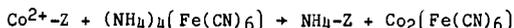
The ZSM-5, with $\text{SiO}_2/\text{Al}_2\text{O}_3 \sim 30$, was synthesized using the procedure given in the patent literature by Argauer and Landolt (10), with minor modifications. The procedure yields ZSM-5 having crystallites approximately one micron in size. The zeolite was calcined in air at 538°C to decompose the tetrapropylammonium (TPA^+)

cation. It was converted to the ammonium form by three successive exchanges using NH_4Cl solution.

To prepare the metal-loaded catalysts, the solution-impregnated method was used. Aqueous cobalt (II) nitrate solution was added to $\text{NH}_4\text{-ZSM-5}$ until incipient wetness was reached. The atmosphere surrounding the mixture was evacuated after the solution was added. The mixture was dried with stirring at 100°C . Three samples with 2.7, 5.9, and 9.0 wt% $\text{Co/NH}_4\text{-ZSM-5}$ were prepared by this method.

In order to prepare a sample of $\text{Co/NH}_4\text{-ZSM-5}$ in which the cobalt could be expected to be almost entirely in the ion-exchanged form, the following procedure was used. Ten grams of $\text{NH}_4\text{-ZSM-5}$ was added to 120 mL of 9.5 wt% $\text{Co(NO)}_3\cdot 6\text{H}_2\text{O}$ solution in water at 90°C . The mixture was stirred for one hour and filtered. The procedure was repeated two more times, and the zeolite sample was thoroughly washed with water until no nitrate was present. The sample had 0.9 wt% Co , presumably in the ion-exchanged form (IE), and will be designated 0.9 wt% $\text{Co/NH}_4\text{-ZSM-5}$ (IE).

"Back-exchange" (BE), i.e., removal of the ion-exchanged Co^{2+} from the zeolite, was attempted on the basis of the following reaction (8):



The $\text{Co}_2(\text{Fe}(\text{CN})_6)$, an insoluble compound, would be distributed throughout the zeolite. Subsequent reduction in hydrogen at 400°C should result in a zeolite containing cobalt and iron, while the zeolite itself is converted to the H-form.

To carry out the back-exchange, 15 g of 0.9 wt% $\text{Co/NH}_4\text{-ZSM-5}$ (IE) was stirred in 150 mL of 3.3 wt% $(\text{NH}_4)_4\text{Fe}(\text{CN})_6\cdot\text{H}_2\text{O}$ solution in water for 4 hours at room temperature. The mixture was filtered. The back-exchanged zeolite sample was analyzed and found to contain 0.9 wt% Co and 0.2 wt% Fe , and will be designated 0.9 wt% Co , 0.2 wt% $\text{Fe/NH}_4\text{-ZSM-5}$ (BE).

A part of each of the five samples was pelleted into 3-mm-diameter tablets for catalytic activity tests. The pellets were calcined in air at 450°C for one hour to convert the $\text{NH}_4\text{-ZSM-5}$ to the H-form. Parallel studies using infrared spectroscopy showed deammoniation was nearly complete under these conditions (7).

(b) Magnetization Measurements

Samples for magnetic analysis were placed in 4-mm-outside-diameter glass tubes and reduced in flowing hydrogen 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 saturation magnetization was obtained by plotting σ versus $1/H$ and extrapolating to zero (infinite fields). The values obtained were compared with the known saturation magnetization of bulk metallic cobalt, and the degree of reduction was obtained. The percent reduction is reported in Table I.

(c) Chemisorption Measurements

Hydrogen adsorption measurements were performed using a conventional glass volumetric adsorption apparatus. One gram of catalyst sample was used. The sample was heated to 200°C ($4^\circ\text{C}/\text{min}$) under flowing He (60 mL/min) and kept at that temperature for 1 hour. The sample chamber was evacuated and cooled to 50°C . Hydrogen (60 mL/min) was introduced and the temperature was raised to 350°C ($4^\circ\text{C}/\text{min}$). The sample was reduced at 350°C for 16 hours. The sample chamber was evacuated to 10^{-5} torr and cooled to the adsorption temperature.

The H₂ adsorption measurements were conducted at 100°C. The adsorption isotherms are shown in Figure 1.

(d) Metal Particle Size Calculations

The values of hydrogen uptake were extrapolated to zero hydrogen pressure from the linear portion of the isotherm (Figure 1), as outlined by other workers for nickel catalysts (11,12).

The metal dispersions $D = \text{Co}_s / \text{Co}_t$, where Co_s is the number of surface cobalt atoms and Co_t is the total number of cobalt atoms, were calculated using the adsorption stoichiometry of $\text{H}/\text{Co}_s = 1$. Average crystallite diameters (Table I) were calculated from $\%D$ for spherical hcp metal crystallites (6) of uniform diameter using the following relation (13):

$$d(\text{nm}) = 73.81/\%D$$

(e) Catalytic Conversion Tests

The equipment used was a downflow, fixed bed reactor of 1-cm inner diameter. The mass of the catalyst sample was 1.35 g. The sample was reduced in hydrogen at 350°C. The conversion of syngas ($\text{H}_2/\text{CO} = 1$) at 280°C, 12 bar, and a flow of 0.659 g/g cat. hr was examined for a 24-hour period.

The products of the reaction were CO_2 , H_2O and hydrocarbons, and were analyzed using gas chromatography. The C_5+ product was analyzed using simulated distillation. It was also separated into aromatics, olefins and saturates using the FIA method.

Ethylene conversion studies were also conducted in a reactor similar to that mentioned above. After treatment with hydrogen at 350°C, the reaction mixture consisting of 30 vol% C_2H_4 and 70 vol% H_2 , was introduced at 1 atm and a flow rate of 0.983 g/g cat. hr. The temperature of the reactor was maintained at 320°C. The products were analyzed as described above.

RESULTS AND DISCUSSION

The results of magnetization and chemisorption studies are shown in Table I, Figure 1, and Figure 2. For the three catalysts containing 9.0, 5.9, and 2.7 wt% Co, approximately 2.2 wt% of the catalyst is the amount of cobalt that has not been reduced to metallic cobalt in flowing hydrogen at 350°C (see Table I). The hydrogen uptake and the degree of reduction exhibit similar trends when plotted against the cobalt loading (Figure 2), and each curve intercepts the horizontal axis at nearly 2.2 wt%.

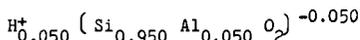
The amount of hydrogen chemisorbed can be expected to be approximately proportional to the metal surface area. The absence of metallic cobalt in a sample would result in zero chemisorption of hydrogen. It is thus understandable that both the hydrogen uptake and the degree of reduction obtained from the magnetization study become vanishingly small at the same concentration (2.2 wt%) of cobalt in the catalyst.

The results from $\text{H}_2 + \text{CO}$ conversion experiments are shown in Figure 2 and Table II. The variation of the rate of conversion with cobalt loading also follows the same trend as the chemisorption and degree of reduction. Of the liquid hydrocarbon products obtained with these catalysts, nearly 95% is in the gasoline boiling range, as revealed by simulated distillation. The C_5+ product consists of aromatics, branched olefins, and branched paraffins, which are constituents of high octane gasoline.

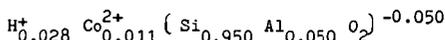
The conversion of H_2+CO by 0.9 wt% Co/ZSM-5 (IE) is zero, consistent with the observation that the degree of reduction is zero after exposure to hydrogen at 350°C (Table I and Figure 2). This provides additional support that the cobalt in this sample is in an ion-exchanged form that cannot be reduced to the catalytically active metallic cobalt. When the sample is back-exchanged to yield 0.9 wt% Co, 0.2 wt% Fe/ZSM-5 (BE), the $CO+H_2$ conversion is 17.3%, and the degree of reduction is 48%. The existence of a ferromagnetic moment indicates that Co (and possibly Fe) is in the metallic state in the back-exchanged sample.

The conversion of ethylene over H-ZSM-5 and the metal-zeolite samples (ion-exchanged and back-exchanged) was used as a method for comparison of their catalytic acid function. The results are shown in Table III for the first six hours on stream. The cobalt-exchanged sample exhibits C_2H_4 conversion of 78.7%, while the H-ZSM-5 (parent sample) exhibits a conversion of 86.1%. The cobalt-exchanged sample also yields a lower fraction of aromatics (37%) in comparison to H-ZSM-5, which yields 53% aromatics in the liquid hydrocarbon product. It is thus indicated that the acid function of the zeolite is weakened by the presence of cobalt in ion-exchanged form. Back-exchange of the cobalt results in a catalyst that brings about an improved ethylene conversion (89.8%) and larger aromatic fraction (42%).

The above results obtained from physical measurements (chemisorption and magnetization) and catalytic activity tests indicate how metal speciation in cobalt/ZSM-5 can be characterized. The parent sample of H-ZSM-5 with $SiO_2/Al_2O_3=38$ can be represented by



The ion-exchanged sample 0.9 wt% Co/ZSM-5 (IE) can be represented by



It can be noticed that 44% of the H^+ sites have been exchanged with cobalt, resulting in weakened acidity. In the back-exchanged sample, at least 48% of Co^{2+} has been replaced by NH_4^+ , while the cobalt is converted to the insoluble compound $Co_2Fe(CN)_6$. Calcination at 450°C, followed by reduction in H_2 at 350°C, results in the conversion of the zeolite to the H^+ -form and the formation of metallic cobalt. The resulting sample exhibits catalytic activity for synthesis gas conversion.

CONCLUDING REMARKS

This study demonstrated that magnetic and chemisorptive techniques can be used to characterize metal speciation in catalysts such as Co/ZSM-5. In particular, the amounts of ion-exchanged cobalt and cobalt external to the zeolite can be estimated. These measurements enable one to interpret the catalytic activity and selectivity of the catalyst.

In our attempts to introduce cobalt in cationic form in ZSM-5 a temperature of 90°C has been used for the exchange with aqueous cobalt nitrate solution. It appears that 0.9 wt% Co can be introduced into ZSM-5 of $SiO_2/Al_2O_3=38$ under these circumstances. Analyses of the Co/ZSM-5 samples that were prepared by impregnation at room temperature with cobalt nitrate solution showed that approximately 2.2 wt% Co was in a form not reducible to metallic cobalt (Table I). In earlier work (6,7), the Co/ZSM-5 samples were subsequently washed with water to yield samples that contained 1.4-1.7 wt% Co. Hence it is possible that exchange at temperatures lower than 90°C would yield samples containing more than 0.9 wt% Co in ion-exchanged form (14).

This study has shown that $\text{Co}^{2+}/\text{ZSM-5}$ can be back-exchanged and reduced to yield metallic cobalt supported on H-ZSM-5. Chemisorption measurements are currently being carried out to determine the degree of dispersion of such samples. The back-exchanged samples are catalytically active in synthesis gas conversion. The method of back-exchange should be generally applicable for preparing metal-zeolite catalysts where it is desirable to free the zeolite of metal cations in order to restore the acidity to its original strength, and to have the metal on the exterior of the zeolite crystallites in a highly dispersed, catalytically active form.

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TABLE I
Results from Magnetization and Chemisorption on Co/ZSM-5

Metal Loading (wt%)	% Reduction in H_2 at 350°C (from magnetization)	Wt% Co Unreduced	H_2 Uptake at 100°C ($\mu\text{ mol g}^{-1}$)	d(nm)
9.0	78	2.0	35.4	12.4
5.9	64	2.1	22.5	10.4
2.7	10	2.5	2.4	8.5
0.9 (IE)	0	0.9		
0.9 (BE) +0.2 Fe	48	0.4		

TABLE II

Conversion and Product Distribution From Co/ZSM-5 Catalysts
During the Initial 24-Hour Period
IE: ion-exchanged; BE: back-exchanged

H₂/CO = 1; P = 21 bar; Temperature = 280°C; Feed Rate = 0.659 g/g cat. hr

Co in Catalyst (wt%)	9.0	5.9	2.7	0.9 (IE)	0.9 (BE) +0.2 Fe
CO Conversion (%)	56.5	54.6	21.0	0.0	13.7
H ₂ Conversion (%)	85.8	80.8	34.3	0.0	20.9
CO+H ₂ Conversion (%)	70.7	67.3	27.4	0.0	17.3
<u>Product Composition (wt%)</u>					
CO ₂	18.6	13.2	8.1		13.9
H ₂ O	46.1	50.9	56.6		55.9
CH _n	35.2	35.8	35.3		30.2
<u>Composition of CH_n (wt%)</u>					
CH ₄	24.4	24.0	33.6		42.4
C ₂ H ₄	0.0	0.4	0.0		0.0
C ₂ H ₆	2.7	2.3	5.2		3.1
C ₃ H ₆	0.8	0.6	0.0		0.0
C ₃ H ₈	2.7	2.7	7.7		18.4
C ₄ H ₈	0.8	1.4	0.9		0.0
C ₄ H ₁₀	5.4	6.6	18.7		24.2
C ₅ +	63.0	61.9	33.8		11.8
<u>Liquid Product Composition (vol%)</u>					
Aromatics	19.5	23.0			
Olefins	32.5	30.5			
Saturates	48.0	46.5			

TABLE III

Conversion of 30 vol% C₂H₄ + 70 vol% H₂ Mixture
over H-ZSM-5 and Co/ZSM-5 (SiO₂/Al₂O₃=38).

Feed Rate = 0.983 g/g cat. hr; Temperature = 320°C

Catalyst	H-ZSM-5	0.9% Co/H-ZSM-5 (ion-exchanged)	0.9% Co, 0.2% Fe/H-ZSM-5 (back-exchanged)
Period (hours)	0-6	0-6	0-6
C ₂ H ₄ Conversion (%)	86.1	78.7	89.8
H ₂ Conversion (%)	9.2	8.5	13.4
<u>Product Composition (wt%)</u>			
CH ₄	0.0	0.0	0.0
C ₂ H ₆	14.5	13.3	27.0
C ₃ H ₆	7.6	12.6	6.1
C ₃ H ₈	5.5	2.5	4.3
C ₄ H ₈	11.6	14.0	9.7
n-C ₄ H ₁₀	5.8	6.3	5.7
i-C ₄ H ₁₀	7.6	5.4	5.7
C ₅ +	47.3	45.8	41.1
<u>Liquid Product Composition</u>			
Aromatics	53	37	42
Olefins	31	50	43
Saturates	16	13	15

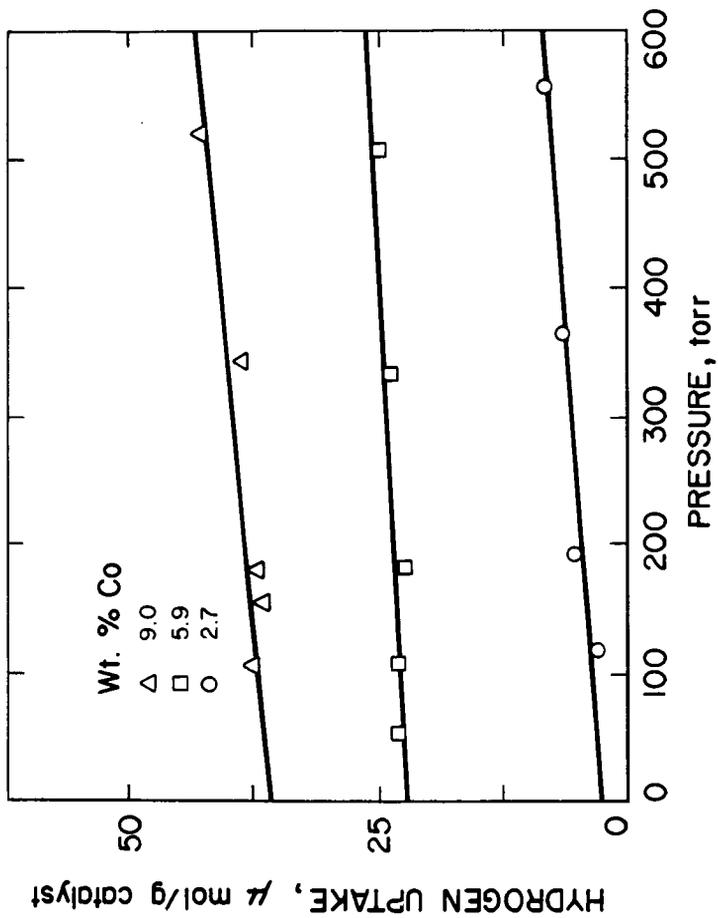


Figure 1. Hydrogen adsorption Isotherms at 100°C on Co/ZSM-5 catalysts.

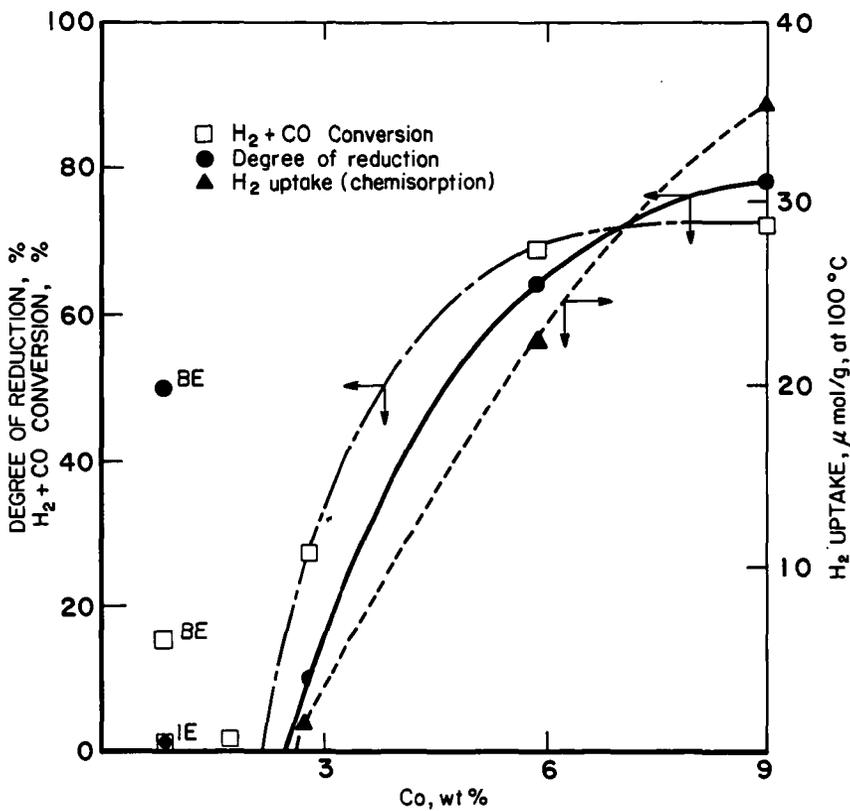


Figure 2. Degree of reduction, chemisorption and H₂ + CO conversion on Co/ZSM-5. IE: ion-exchanged, BE: back-exchanged.

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