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Dual Cobalt Speciation in Co/ZSM-5 Catalysts[1]

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X-Ray diffraction, X-ray photoelectron spectroscopy, and infrared spectroscopy are used to investigate cobalt speciation in Co/ZSM-5 catalysts containing 1.4 to 9.5 wt% cobalt. These catalysts, metal-impregnated using incipient wetness techniques with $Co(NO_3)_2 \cdot 6H_2O$, are shown to contain highly dispersed, ion-exchanged, non-reducible Co^{2+} species interior to the ZSM-5, and large, reducible cobalt oxide crystallites on the exterior of the ZSM-5 crystallite surface. The number of Co^{2+} ions located inside a unit cell of ZSM-5 and the number of pyridine molecules that coordinately bond to each of these ions are estimated by using infrared data characterizing pyridine chemisorption. The crystalline forms of cobalt on the surface of the ZSM-5 are identified and their sizes estimated after O_2 calcination, H_2 reduction, and CO + H_2 exposure. These data are then scrutinized for correlations of chemical and physical properties of the Co/ZSM-5 catalysts with conversion activity and selectivity for synthesis of hydrocarbons from CO + H_2 gas.

INTRODUCTION

The preparation of synthesis gas conversion catalysts, Co/ZSM-5, by impregnation of aqueous or acetone solutions of cobalt nitrate incorporates some cobalt into the interior of the ZSM-5 crystallites (*1*, *2*). This incorporation is the result of ion exchange of H^+ by ionic cobalt, the oxidation state of which has not been firmly identified. If the amount of cobalt interior to the ZSM-5 channels is limited by an ion-exchange capacity, the maximal amount of cobalt able to be incorporated into the zeolite can be calculated knowing its Si/Al atomic ratio. Thereby, assuming a 1 : 1 ratio between the number of H^+ and aluminum in H^+–ZSM-5 and the exchange of $2H^+$ for Co^{2+}, a maximum of four Co^{2+} ions could be incorporated per ZSM-5 unit cell for the catalysts described herein with Si/Al = 11. This concentration is approximately 4 wt% of the ZSM-5. Such a concentration has not been obtained to date, since infrared results have shown that Brønsted acid sites still exist when the Co/ZSM-5 catalysts contain as much as 9 wt% cobalt (*1*, *2*). The present study discusses these Co/ZSM-5 catalysts and shows that they contain a dual cobalt speciation consisting of (1) finely dispersed cobalt interior to the ZSM-5 crystallites, the amount of which can be estimated from infrared data, and (2) large cobalt crystallites exterior to the ZSM-5 crystallites. This discussion includes surface and bulk characterization of the catalysts after catalyst synthesis, calcination, reduction, and exposure to 1 : 1 CO + H_2 synthesis gas, in addition to microreactor activity testing for the conversion activity of 1 : 1 CO + H_2 to hydrocarbons.

The interaction of iron with ZSM-5 depends upon the method of impregnation (*1*, *2*). As a result of these previous studies, it was believed that Co/ZSM-5 catalysts could be prepared with cobalt on only the external crystallite surface of ZSM-5 or entirely interior to its pore structure. These

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[1] 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.

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preparations are discussed herein, along with the identification of the cobalt species that are formed during these preparations. Such identification is then used to examine the results of microreactor tests for the conversion of 1 : 1 CO + H_2 to hydrocarbons.

EXPERIMENTAL

Catalyst preparation. The ZSM-5 support was prepared using techniques described in the literature (*3*). It was converted into the ammonium form by ion exchange using NH_4Cl solution. Atomic absorption (AA) techniques were used to identify its Si and Al concentration, with a resultant Si/Al = 11. The degree of crystallinity, as estimated by X-ray diffraction, was 80%. Aqueous solutions of cobalt(II) nitrate were loaded onto NH_4^+–ZSM-5 by incipient wetness impregnation techniques to produce catalysts containing 2.8, 5.1, 7.3, and 9.5 wt% cobalt as determined by AA. These catalysts will be designated 2.8% Co/ZSM-5/AQ, 5.1% Co/ZSM-5/AQ, 7.3% Co/ZSM-5/AQ, and 9.5% Co/ZSM-5/AQ.

Two other catalysts were prepared from those listed above. These were obtained by washing the as-synthesized catalysts containing 5.1 and 7.3% cobalt prior to calcination—and hence still containing cobalt nitrate—in copious quantities of distilled H_2O. This washing was done in successive batches until the water solution after washing no longer contained a pink coloration typical of hydrated cobalt nitrate. The resultant Co/ZSM-5 catalysts prepared by this procedure contained approximately 1.4 wt% cobalt irrespective of whether the starting parent catalyst contained 5.1 or 7.3% cobalt. In the remainder of this manuscript, catalysts prepared thus shall be described as 1.4% Co/ZSM-5/W. Two more catalysts were prepared by physically mixing precipitated Co_3O_4 with the ZSM-5; these catalysts will be designated 8.5% Co/ZSM-5/PM and 1.6% Co/ZSM-5/PM.

Characterization. Samples for infrared (ir) and X-ray photoelectron spectroscopy (XPS) analyses were prepared by pressing approximately 20–30 mg of the catalysts into thin wafers using a 13-mm-diameter die. The cell and techniques used during ir data acquisition of chemisorbed pyridine have been described (*1, 2*). The ir data were obtained on catalysts that had been calcined in flowing O_2 at 450°C or calcined and then reduced with flowing H_2 at 450°C, followed by evacuation for at least 1 h. The chemisorption of pyridine was done by exposing the catalysts to pyridine vapor at several millimeters of pressure for 1 h at 150°C and then evacuating for 1 h at the same temperature. A Perkin–Elmer 180 spectrophotometer was used for data acquisition; frequencies reported herein are repeatable to within $\pm 2\ \mathrm{cm}^{-1}$, while the precision of intensity ratios is approximately ±15%.

The XPS data were acquired on McPherson ESCA 36 and AEI ES200A electron spectrometers equipped with Mg anodes ($MgK\alpha$ = 1253.6 eV). All binding energies were corrected for charging by assuming the binding energy of the carbon 1*s* band to be 284.6 eV. The baseline pressure in the XPS chambers during spectral acquisition was 5×10^{-6} Pa. The XPS analyses of reduced Co/ZSM-5 samples was also accomplished. These studies were facilitated by use of a specially designed sample probe, similar to that described by Patterson *et al.* (*4*), that can be placed in a tubular furnace during treatment of the catalysts. The sample probe can then be transferred to the XPS vacuum chamber for spectral acquisition from the samples without exposing them to atmospheric conditions.

Because of weak XRD signals from the cobalt and interference from ZSM-5, XRD data could only be obtained from 7.3% Co/ZSM-5/AQ and 9.5% Co/ZSM-5/AQ. These XRD spectra were acquired on a Picker X-ray diffractometer outfitted with a single bent graphite, diffracted beam monochromator. These data were obtained using a Cu source operated at 35 kV and 15 mA, and by step scanning through 2θ angles with (1/

30)° increments. An *in situ* camera attachment enabled XRD data to be obtained from the same volume of material in the H_2 reduced, O_2 oxidized, and CO + H_2 exposed catalysts. Subtraction of the ZSM-5 spectrum from that of Co/ZSM-5 was accomplished by Fourier-unfolding the ZSM-5 spectrum from that of Co/ZSM-5 (*5*). This technique provided cobalt peaks with definition suitable for crystallite size analysis. Size analysis involved measurement of the unfolded breadths at half intensity for Bragg diffraction from the (002), (101), and (100) planes of hexagonal close packed (hcp) cobalt.

Activity evaluation. The catalysts were pressed into ⅛-inch-diameter pellets and reduced under H_2 at 300 psig and 350°C for 24 h. Catalytic data were obtained by using a Chemical Data Systems, Inc., Series 810 Continuous Flow-High Pressure microreactor system. Conditions employed were 300 psig pressure of 1 : 1 synthesis gas, a GHSV of 1000 h^{-1}, and a reactor temperature of 280°C. The products were mainly CO_2, H_2O, and hydrocarbons. A hot trap at 175°C collected wax and heavy oil. It was followed by a cold trap at 0°C which collected water, gasoline range products, and light oil. Samples of the exiting gas were 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 into aqueous and hydrocarbon fractions. The hydrocarbon product was analyzed by simulated distillation. It was also separated into aromatics, olefins, and saturates using FIA chromatography.

RESULTS

The XRD patterns of ZSM-5 and 9.5% Co/ZSM-5/AQ after H_2 reduction at 350°C are shown in Figs. 1a and b, respectively. These complex spectra are the result of the many peaks associated with orthorhombic ZSM-5. To obtain well-defined peaks associated with cobalt and/or cobalt compounds, the ZSM-5 spectrum has to be subtracted from that of the Co/ZSM-5. This subtraction can be accomplished by Fourier-unfolding the ZSM-5 spectrum from the Co/ZSM-5 spectrum. The unfolding technique, developed specifically to obtain the cobalt spectrum, is discussed elsewhere (*5*). After unfolding, the data shown in Fig. 1 produce the peaks shown in Fig. 2. These peaks can be identified as the (100), (002), and (101) Bragg planes from hexagonal cobalt and the (111) and (200) peaks from CoO. The crystallite size of the cobalt calculated from the (002) peak breadth is 29.6 nm, while a 23.5-nm size was obtained from the (100) peak. Both the (002) and the (100) peak breadths are not affected by faults on the basal plane, while the breadth of the (101) is affected by the existence of basal plane faults (*6*). A 3.9-nm particle size determined from the (101) indicates that faults exist in the cobalt particles, since the plane affected by faults gives a much smaller cobalt particle size than those not affected. A summary of the particle sizes

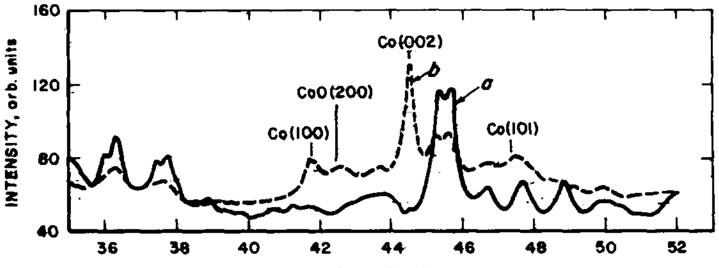

FIG. 1. The X-ray diffraction pattern of (a) ZSM-5 (SiO_2/Al_2O_3 = 22) and (b) 9.5% Co/ZSM-5/AQ after H_2 reduction at 350°C for 16 h.

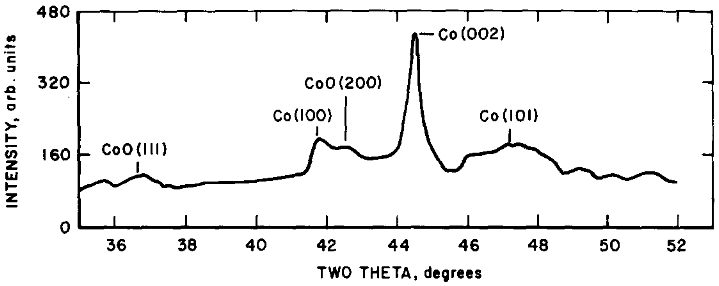

FIG. 2. The X-ray diffraction pattern obtained after Fourier unfolding of the pattern of H_2 reduced ZSM-5 from that of 9.5% Co/ZSM-5/AQ. The peaks labeled (100), (002), and (101) are from hcp cobalt metal, and (111) and (200) are from CoO.

measured from the hexagonal cobalt is presented in Table 1. These data show that no significant change in particle size occurs during prolonged reduction times under hydrogen at 350°C. After CO + H_2 exposure at 280°C for 24 h, the XRD patterns for the (100), (101), and (002) Bragg planes were the same as shown in Fig. 2. Cobalt oxide, CoO, is also observed to exist in reduced and CO + H_2 exposed catalysts. The crystallite size of this oxide is approximately 9.0 nm. No cobalt carbide is detected if the temperature of the catalysts is maintained below 320°C during CO + H_2 exposure.

The XPS spectrum of the Co 2*p* region from 5.1% Co/ZSM-5/AQ in its as-synthesized nitrate form and after 150°C calcination is shown in Fig. 3. The binding energy of the Co $2p_{3/2}$ peak in the as-synthesized catalyst is 782.0 ± 0.3 eV. A separation of approximately 15.7 eV is found for $2p_{1/2}$–$2p_{3/2}$. An intense shoulder appears approximately 5.0 eV above the Co $2p_{3/2}$ peak for the as-synthesized catalyst; this shoulder is indicated by the vertical line in Fig. 3. In the calcined catalyst, Fig. 3b, the shoulder on the 781.1-eV, $2p_{3/2}$ peak is less intense than found in the as-synthesized catalyst,

TABLE 1

Summary of X-Ray Diffraction Data for 9.5% Co/ZSM-5/AQ

Treatment	Cobalt species	Particle size (nm)		
		(002)	(101)	(100)
200°C—Calcined, 1 h	Co_3O_4		27.8–41.2	
350°C—Reduced, 2 h	hcp metal + CoO	23.9	3.9	23.5
350°C—Reduced, 6 h	hcp metal + CoO	23.9	3.9	32.4
350°C—Reduced, 24 h	hcp metal + CoO	25.5	3.9	25.5
280°C—CO + H_2, 2 h	hcp metal + CoO	22.6		
280°C—CO + H_2, 22 h	hcp metal + CoO	22.6		

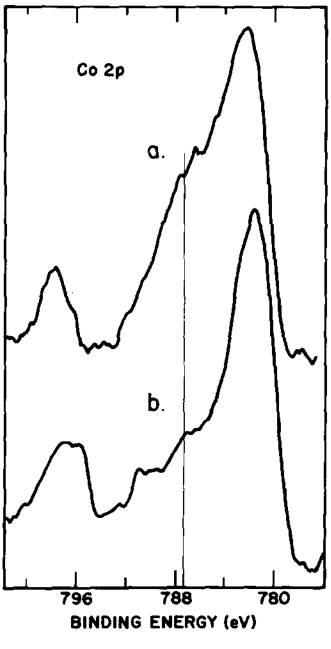

FIG. 3. The XPS spectra of the Co 2*p* region for 5.1% Co/ZSM-5/AQ (a) in its as-synthesized state still while containing $Co(NO_3)_2 \cdot 6H_2O$, and (b) after 150°C calcination in air.

and it is separated from the $2p_{3/2}$ peak by approximately 5.8 eV. The separation $2p_{1/2}$–$2p_{3/2}$ is 15.0 eV in this calcined catalyst.

The XPS spectrum of the Co $2p_{3/2}$ region for 1.4% Co/ZSM-5/W after 100°C drying in air is shown in Fig. 4a; calcination of this catalyst at 450°C does not alter the XPS spectrum from that shown. This spectrum has a peak maximum centered at approximately 783.4 eV, a value 1 to 2 eV greater than that of the spectra in Fig. 3. The spectrum in Fig. 4a also contains a repeatable, complex structure that coincides in binding energy with the Co $2p_{3/2}$ peaks of the XPS spectrum of 450°C H_2-reduced 1.4% Co/ZSM-5/W shown in Fig. 4b. In particular, the center of the maximum of the spectrum in Fig. 4b occurs at approximately 782.4 ± 0.4 eV. The low binding energy side of the Co $2p_{3/2}$ peak for the reduced 1.4% Co/ZSM-5/W catalyst does not contain discrete bands below 781.5 eV but rather a broad and tailing structure. The positions of Co $2p_{3/2}$ peaks for Co_3O_4 (781 eV) and for cobalt metal (778 eV), and a shoulder at 787 eV are indicated by vertical lines in Fig. 4. These reference positions show that the cobalt peak positions are significantly different from those in Fig. 3, and as can be noted by the differences in peak shapes between those in Figs. 3 and 4, the Co/ZSM-5/W catalyst must contain detectable speciation completely different from that observed by XPS in the 5.1% Co/ZSM-5/AQ catalyst. Similar results have been observed for the 7.3% Co/ZSM-5/AQ catalyst and its Co/ZSM-5/W component.

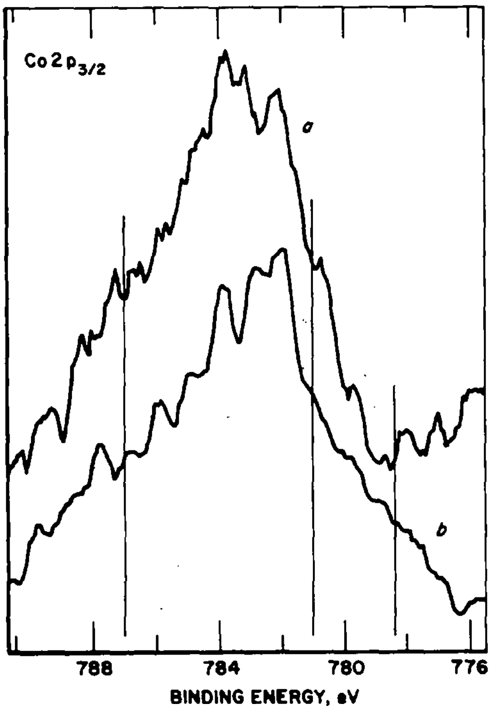

FIG. 4. The XPS spectra of the Co 2p region for 1.4% Co/ZSM-5/W after (a) air drying at 100°C for 16 h and (b) H_2 reduction at 450°C for 4 h.

Infrared spectra of chemisorbed pyridine on a 1.4% Co/ZSM-5/W catalyst after it had been calcined and reduced are shown in Fig. 5. Comparison of the ratio (I_B/I_L) of intensities (*I*) for the Brønsted (B) and Lewis (L) infrared peaks at ca. 1550 and 1450 cm^{-1}, respectively, with previously published spectra (*1*, *2*) shows that I_B/I_L is similar for the washed and parent Co/ZSM-5/AQ catalysts independent of whether the sample was calcined or reduced. The frequencies of the bands for chemisorbed pyridine and associated intensity ratios from infrared studies of these catalysts prepared by aqueous metal nitrate impregnation are shown in Table 2.

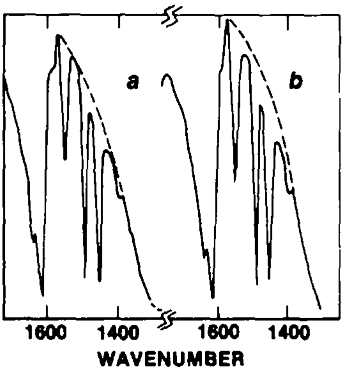

FIG. 5. Infrared spectra of pyridine chemisorbed on 1.4% Co/ZSM-5/W (a) after 450°C calcination of the catalyst in O_2, and (b) after 450°C reduction of the catalyst in H_2.

TABLE 2

Co/ZSM-5 Catalysts Studied by Acquisition of Infrared Spectra of Chemisorbed Pyridine

Catalyst	Pretreatment	Brønsted band (cm^{-1})	Lewis band (cm^{-1})	I_B/I_L
ZSM-5	Calcined	1547	1454	1.74
ZSM-5	Reduced	1547	1454	1.74
2.8% Co/ZSM-5/AQ	Calcined	1548	1453	0.24
5.1% Co/ZSM-5/AQ	Calcined	1545	1450	0.27
1.4% Co/ZSM-5/W	Calcined	1548	1450	0.17
1.4% Co/ZSM-5/W	Reduced	1548	1450	0.22

Note. The ratio I_B/I_L is the intensity of the Brønsted peak divided by that of the Lewis peak.

DISCUSSION

Characterization

The equivalence, within experimental error, of the I_B/I_L ratios for the Co/ZSM-5/AQ catalysts independent of cobalt concentration (Table 2) indicates that only a portion of the total amount of cobalt causes modification of the acidity of ZSM-5 in the 5.1% Co/ZSM-5/AQ catalyst. This modification is the result of ion exchange of a fraction of the total amount of cobalt for H^+ in ZSM-5, as has been previously discussed (*1, 2*). To determine the amount of ion exchange, the intensity ratios I_B/I_L from infrared analysis, the SiO_2/Al_2O_3 ratio of the ZSM-5, and the ionic form of the ion-exchanged cobalt have to be integrated with fundamental equations governing Lewis acid site formation during calcination of the ZSM-5 and governing ion exchange during cobalt impregnation.

First, the ionic state of cobalt in these Co/ZSM-5 catalysts will be discussed to determine the form of the ion-exchanged species. The XPS spectrum of the Co $2p$ region for the as-synthesized, nitrate-containing, Co/ZSM-5 catalyst in Fig. 3a indicates that Co^{2+} species are present, since the main $2p_{3/2}$ peak has a binding energy similar to that for cobalt nitrate, and it has an intense shoulder at 787 eV (*7, 8*). In addition, the $2p_{1/2}$–$2p_{3/2}$ spin-orbit splitting of 15.7 eV for this catalyst suggests Co^{2+} species (*7, 8*). After calcination at 150°C, the relative intensity of the 787 eV shoulder decreases, and the $2p_{1/2}$–$2p_{3/2}$ splitting decreases to 15 eV. These results suggest less intensity contributions to the XPS spectrum from Co^{2+} species and more from Co^{3+}. The XRD measurements confirm this interpretation by showing that calcined Co/ZSM-5/AQ catalysts contain large Co_3O_4 crystallites. Since Co_3O_4 contains two Co^{3+} for every Co^{2+}, the influence of Co^{2+} in the XPS spectra of the calcined catalyst in Fig. 3b should be greatly decreased from that observed in the spectra of as-synthesized catalysts, Fig. 3a; hence, the intensity of the 787 eV shoulder should be less in the calcined catalyst than in the as-synthesized catalyst. This is observed. However, the 34.5-nm-sized Co_3O_4 crystallites will be located on the exterior of the ZSM-5 crystallites, not inside the 0.6-nm channels of the ZSM-5.

Large cobalt crystallites are not present on the 1.4% Co/ZSM-5/W catalyst and, as a result, will not shield detection of cobalt interior to the ZSM-5 during XPS measurements on this catalyst. Hence, possible detection of the cobalt speciation inside of ZSM-5 should be enhanced with the Co/ZSM-5/W catalysts relative to the Co/ZSM-5/AQ catalysts. Additionally, as shown in Fig. 5 and Table 2, the 1.4% Co/ZSM-5/W catalyst contains a Brønsted-to-Lewis intensity ratio (I_B/I_L) equal to that found in the Co/ZSM-5/AQ catalysts. Thus, the proportion of ion-exchanged cobalt relative to the total amount of cobalt is greatly increased in the washed catalysts. However, the XPS spectra of 1.4% Co/ZSM-5/W are somewhat unusual and cannot be interpreted unambiguously. The higher-than-normal binding energy of the most intense band in Fig. 4a at 783.4 eV is suggestive of cobalt in a highly oxidized environment, as has recently been discussed for Ru in NaY-zeolite (*9*). Reduction decreases only slightly the intensity at 783.4 eV and shifts the center of the Co $2p_{3/2}$ band to 782.7 eV.

This position is higher than that expected for normal ionic species of Co^{2+} or Co^{3+} (*7, 8*). In addition, a very small amount of cobalt metal is formed during reduction at 450°C, whereas magnetic measurements of 5.1% Co/ZSM-5/AQ and 7.3% Co/ZSM-5/AQ after 350°C reduction show 60 to 70% metallic cobalt (*10*). This percentage of reduction can also be observed in the XRD data shown in Fig. 2. That portion of cobalt reduced to a metallic species in the 1.4% Co/ZSM-5/W catalyst may be on the exterior of the ZSM-5 crystallites in the form of small crystallites.

The XPS spectra of 1.4% Co/ZSM-5/W contain a significantly intense shoulder near 787 eV. This intensity suggests that bare Co^{2+} species exist as the ion-exchanged form of cobalt in the ZSM-5. Other possibilities also exist, for example, a $[Co^{2+}(OH)]^+$ species. This form of cobalt could also produce an intense shoulder near 787 eV. However, such a cobalt hydroxyl species would not be expected to increase the number of Lewis acid sites in the ZSM-5 but instead would create protonic sites similar to those in H^+–ZSM-5. Other arguments that are presented below also suggest that $[Co^{2+}(OH)]^+$ is not the ion-exchanged form of cobalt. Thus, two major cobalt species exist in the Co/ZSM-5/AQ catalysts. On the external surface of the ZSM-5 crystallites are large cobalt-containing crystallites that reduce to cobalt metal and CoO at 350°C. Interior to the ZSM-5 are highly dispersed Co^{2+} species in an ion-exchanged form that does not reduce to cobalt metal at 450°C. Remnants of externally located cobalt are expected to cause the other species discussed for 1.4% Co/ZSM-5/W.

To calculate the amount of ion exchange that occurs during cobalt nitrate impregnation onto ZSM-5, the infrared data in Table 2 have to be integrated with fundamental properties of the ZSM-5. For this calculation it is assumed that the non-acidic form of ZSM-5, NH_4^+–ZSM-5, has been activated in such a way as to create only protonic sites; such ZSM-5 has been made by controlled calcination of highly crystalline NH_4^+–ZSM-5 (*11*). In our laboratory, the controlled calcination of Fe/ZSM-5/EX catalysts at 300°C has also produced only protonic sites (*12*); however, the infrared spectral region near 1450 cm^{-1} showed that NH_4^+–ZSM-5 had not been completely transformed into H^+–ZSM-5 by this treatment. This result implies that creation of only protonic acidity by controlled calcination may not produce the maximal concentration of protonic acid sites. For purposes of the following calculation, the calcined ZSM-5 is assumed to contain maximum Brønsted acidity. In such a case and with $SiO_2/Al_2O_3 = 22$, the number of Brønsted acid sites per unit cell, N_B, would be equal to the number of acid sites per unit cell, N. This number will depend on the number of aluminum atoms per unit cell, N_{Al}, which for $SiO_2/Al_2O_3 = 22$ will be eight, i.e.,

$$N = N_B = N_{Al} = 8 \qquad (1)$$

Simultaneously, $N_L = 0$, where N_L is the number of Lewis sites per unit cell. Upon calcination of the ZSM-5 at a sufficiently high temperature to create H^+–ZSM-5, Lewis acid sites will be created by dehydroxylation; such a process requires that for each Lewis acid site created, two Brønsted sites have to be destroyed. Hence, denoting numbers of acid sites in H^+–ZSM-5 by primed symbols, the following set of equations is obtained:

$$N' = N'_B + N'_L \qquad (2)$$

$$N'_B = N - 2N'_L = 8 - 2N'_L \qquad (3)$$

From Table 2, the Brønsted-to-Lewis intensity ratio for the calcined or reduced ZSM-5 used in this study is $I_B/I_L = 1.74$. (In the present context, this ratio would be more appropriately labeled $I'_B/I'_L = 1.74$.) As a result of assuming that the relative absorption coefficient associated with the Lewis and Brønsted acid sites in ZSM-5 is similar to that in mordenite, i.e., $\varepsilon_L/\varepsilon_B = 1.5$ (*1, 13, 14*), and of assuming that $N'_B/N'_L = (\varepsilon_L/$

$\varepsilon_B) I'_B/I'_L$, the ratio N'_B/N'_L becomes the following:

$$N'_B/N'_L = 2.6 \qquad (4)$$

Combining Eqs. (2), (3), and (4) gives the number of Brønsted and Lewis acid sites per unit cell for the H^+–ZSM-5 of $N'_B = 4.52$ and $N'_L = 1.74$. Hence, $N' = N'_B + N'_L = 6.26$.

Infrared results on the chemisorption of pyridine show that cobalt impregnation changes the Brønsted-to-Lewis acidity distribution. The resulting distribution is governed by a set of equations similar to those in Eqs. (2) and (3). Denoting the numbers of acid sites per unit cell in 1.4% Co/ZSM-5/W by double primes, the following equations are found:

$$N'' = N''_B + N''_L \qquad (5)$$

$$N''_L = N''_{Co} + N''_{Al} = N''_{Co} + N'_L \qquad (6)$$

where N''_{Co} is the number of Lewis sites per unit cell associated with cobalt, and N''_{Al} is the number of Lewis sites associated with aluminum, and it is assumed that no aluminum sites are lost or created during cobalt impregnation. Combining Eqs. (5) and (6) gives the following:

$$N'' = N''_B + N''_{Co} + 1.74 \qquad (7)$$

If Co^{2+} ions exchange for $2H^+$, the number of Brønsted sites destroyed should equal twice the number of cobalt ions involved in ion exchange:

$$N'_B - N''_B = 2N''_{Co} \qquad (8)$$

Since

$$N''_B/N''_L = \frac{N''_B}{N''_{Al} + N''_{Co}} = \frac{N''_B}{N'_L + N''_{Co}} = 0.3 \qquad (9)$$

for reduced or calcined Co/ZSM-5-W, the combining of Eqs. (8) and (9) gives the following:

$$\frac{N'_B - 2N''_{Co}}{N'_L + N''_{Co}} = 0.3 \qquad (10)$$

Then, substituting the values for N'_B and N'_L permits the calculation of N''_{Co}, N''_B, N''_L, and N''; these values are $N''_{Co} = 1.74$, $N''_B = 1.04$, $N''_L = 3.48$, and $N'' = 4.52$ for 1 Py/Co^{2+}.

A value of 1.74 for N''_{Co} is approximately 1.65 wt% cobalt. This is in reasonable agreement with the 1.4 wt% AA measured concentration of cobalt in the 1.4% Co/ZSM-5/W catalyst. However, the above calculation assumed that one pyridine was adsorbed per Co^{2+}. Such an assumption, though reasonable, is not the only possibility. For example, two pyridine molecules could possibly be adsorbed per Co^{2+}; more than two may be sterically hindered by channel size restrictions of the ZSM-5. In this case, a calculation similar to Eqs. (6) through (10), with Eq. (6) modified to reflect the adsorption of two molecules per Co^{2+}, i.e., $N''_L = 2N''_{Co} + N''_{Al} = 2N''_{Co} + N'_L$, will give the number of Co^{2+} within the channels of ZSM-5. With such an adaption, the following values are obtained: $N''_{Co} = 1.54$, $N''_B = 1.44$, $N''_L = 4.82$, and $N''_L = 6.26$ for 2Py/Co^{2+}.

A value $N''_{Co} = 1.54$ translates into approximately 1.46 wt% cobalt. This value is slightly closer to the known 1.4 wt% cobalt than that calculated when only one pyridine molecule was assumed to be chemisorbed per Co^{2+} ion. Additionally, with two pyridine molecules per Co^{2+}, $N'' = N' = 6.26$, i.e., the number of pyridine molecules calculated to be adsorbed per unit cell is identical in calcined ZSM-5 or in Co/ZSM-5. No data exist at the present time to determine quantitatively whether the total amount of chemisorbed pyridine remains constant as ion exchange occurs in ZSM-5. If it is the same in H^+–ZSM-5 as in cobalt ion-exchanged ZSM-5, the above calculation shows that two pyridine molecules would be chemisorbed per Co^{2+} ion.

The XPS data suggest that some of the cobalt in the 1.4% Co/ZSM-5/W catalysts is on the surface of the ZSM-5 and not in an ion-exchanged form. A rough estimate of the amount of this externally located cobalt can be obtained from the XPS data of H_2 exposed 1.4% Co/ZSM-5/W by assuming that the portion of cobalt reducible to metallic species is not ion-exchanged. With this assumption, at least 80% of the cobalt is expected to be in ion-exchanged form. This estimate would then decrease the extent of agreement between the actual and calculated amounts of ion exchange. Such a discrepancy may be the result of Lewis acidity contributed by some amorphous silica–alumina phase, as discussed in the previously reported data on ZSM-5 from this laboratory (*1*, *2*), or due to a non-maximal concentration of Brønsted acid sites in the H^+–ZSM-5 used as a reference for obtaining intensity ratios in the above calculations.

The speciation of cobalt on the external surface of ZSM-5 between approximately 5 and 10% cobalt loading is, according to XPS and XRD data, independent of cobalt concentration. Sintering of this cobalt does not occur during prolonged reduction periods (see Table 1), and calcination in oxygen or atmosphere is sufficient to recreate Co_3O_4 crystallites after H_2 reduction and H_2 + CO exposure. Absence of cobalt carbide during 1 : 1 CO + H_2 exposure suggests that such a carbide is not important in CO reduction over cobalt as has been proposed for iron-containing catalysts (*15*). However, this H_2 + CO exposure does increase the amount of CoO species, the importance of which in catalytic reactions is yet unclear.

TABLE 3

Microreactor Results on Conversion and Product Distribution from Co/ZSM-5 Catalysts

	1.4% Co/ZSM-5/W	7.3% Co/ZSM-5/AQ (Metal nitrate impregnation)	8.5% Co/ZSM-5/PM (Physical mixture)	1.6% Co/ZSM-5/PM (Physical mixture)
CO Conversion	Trace	56.5	55.0	19.9
H_2 Conversion	Trace	85.8	66.5	32.4
Product composition (wt%)				
CO_2	0	18.6	12.0	12.0
H_2O	0	46.1	51.3	52.3
CH_n	Trace	35.2	36.6	35.7
Composition of CH_n (wt%)				
CH_4	Trace	24.4	31.2	37.2
C_2H_4	0	0.0	0.0	0.0
C_2H_6	Trace	2.7	3.9	3.9
C_3H_6	0	0.8	0.0	0.0
C_3H_8	Trace	2.7	7.1	13.4
C_4H_8	0	0.8	0.0	0.0
C_4H_{10}	Trace	5.4	15.7	25.2
C_5^+	Trace	63.3	42.0	20.3
Aromatics	[a]	12.1	19.9	[a]
Liquid product composition (vol%)				
Aromatics	[a]	19.5	48.5	[a]
Olefins	[a]	32.5	0.5	[a]
Saturates	[a]	48.0	51.0	[a]

Note. $H_2/CO = 1$; $P = 21$ atm, $T = 280°C$ Feed Rate, GHSV = 1000 h^{-1}.

[a] Quantity too small for FIA analysis.

Catalytic Testing

Table 3 summarizes the catalytic data for the conversion of 1 : 1 CO + H_2 synthesis gas at 280°C over four different Co/ZSM-5 catalysts during a 0- to 24-h test. These data show that when the cobalt is primarily in the interior of the ZSM-5, as for Co/ZSM-5/W samples, the activity for conversion of synthesis gas is negligible. Thus, the ionic Co^{2+} species interior to the ZSM-5 is not active for CO hydrogenation. When the same amount of cobalt (column 4 of Table 3) is physically admixed with ZSM-5, the resultant sample shows significant catalytic activity. The Co/ZSM-5 catalysts containing cobalt exterior and interior to the ZSM-5 crystallites, as in the parent 7.3% Co/ZSM-5/AQ catalyst prepared by metal nitrate impregnation, also have reasonable conversion activity. Presumably the cobalt exterior to the ZSM-5, in its partially reduced state, is the active location for initiation of CO reduction and hydrogenation. In the third column of this table, describing activity for Co/ZSM-5 prepared by physically mixing precipitated Co_3O_4 with ZSM-5, the conversion activity is similar to that found for Co/ZSM-5/AQ. However, the aromatic content of the liquid product is larger from 8.5% Co/ZSM-5/PM than from 7.3% Co/ZSM-5/AQ. This difference is ascribed to the inability of cobalt to ion-exchange for H^+ during preparation of this physically mixed catalyst and, hence, to its high Brønsted-to-Lewis acidity ratio. Inability to ion exchange has also been observed in physically mixed Fe/ZSM-5 catalysts (*2*). Therefore, the Brønsted acid sites are responsible for aromatization of the primarily olefinic compounds produced on the cobalt crystallites exterior to the ZSM-5.

CONCLUSIONS

The use of surface sensitive and bulk experimental techniques has enabled the differentiation of two distinct cobalt species in Co/ZSM-5 catalysts. Cobalt interior to the ZSM-5 is in an irreducible, ionic Co^{2+} form created during ion exchange for H^+. Cobalt exterior to the ZSM-5 is in the form of large Co_3O_4 crystallites that are reducible under H_2 at 350°C to hcp cobalt metal and CoO. By varying the preparation methods, either of these cobalt forms can be obtained. It may now be of interest to study the conversion of other reactants over these types of catalysts and possibly to investigate the effect of particle size of the exterior-located cobalt on CO + H_2 conversion activity and selectivity.

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