SPECTROSCOPIC STUDIES OF METAL/ZEOLITE CATALYSIS MATERIALS AND PRODUCTS

By

John M. Stencel

The bifunctional catalysts Co/ZSM-5 and Fe/ZSM-5 are known to be capable of converting synthesis gas (CO + H_2) to a hydrocarbon product that has a carbon number cut-off at approximately C_{12}. The product selectivity in the C_5 to C_{12} range is dependent on catalyst preparation techniques, catalyst activation procedures, and reactor conditions. This paper will discuss the effects of catalyst preparation on the product selectivity by investigating the acidity of the zeolite with infrared monitoring of chemisorbed pyridine. A formulism will be developed to estimate the concentration of metal ions interior to the channels of the ZSM-5 and data will be discussed to determine the oxidation state and association of this metal. In addition, preliminary results on the labile nature of the acidic protons in ZSM-5 will be presented.

The ZSM-5 support was prepared using techniques described in the literature. Aqueous solutions (AQ) of cobalt (II) nitrate or iron (III) nitrate were loaded onto NH_4^+-ZSM-5 by incipient wetness impregnation techniques. The Co/ZSM-5 and Fe/ZSM-5 catalysts were also prepared by carbonyl extraction (CE) of $Co_2(CO)_8$ and $Fe_3(CO)_{12}$ onto the ZSM-5. These catalysts will be designated as Co/ZSM-5/AQ, Fe/ZSM-5/AQ, Co/ZSM-5/CE, and Fe/ZSM-5/CE, respectively. Samples from Co/ZSM-5/AQ were also prepared by successively washing these catalysts in distilled H_2O before heated decomposition of the cobalt nitrate; these samples will be designated Co/ZSM-5/W. The samples for infrared (IR) analyses of chemisorbed pyridine and of adsorbed H_2O or He were prepared by pressing 20-30 mg of the catalysts into thin, self-supporting wafers. Surface sensitive techniques, including ion scattering spectrometry (ISS) and X-ray photoelectron spectroscopy (XPS) were used to monitor concentration of metals on the surface of the ZSM-5 and to determine oxidation states of the metals.

The ratio (I_B/I_L) of intensities (I) for the Bronsted (B) and Lewis (L) infrared peaks at ca. 1550 cm^{-1} and 1450 cm^{-1}, resepectively, after pyridine chemisorption are listed in Table 1. This comparison of I_B/I_L ratios shows that I_B/I_L is similar for the washed or parent Co/ZSM-5/AQ, Fe/ZSM-5/AQ, and Co/ZSM-5/CE. However, the I_B/I_L ratio for Fe/ZSM-5/CE after O_2 calcination is similar to that for ZSM-5; after H_2 reduction of Fe/ZSM-5/CE the I_B/I_L ratio decreases to a value similar to that in the other metal/ZSM-5 catalysts.

The XPS characterization of Co/ZSM-5/AQ after O_2 calcination indicates that the Co is in a combination of Co^{2+} and Co^{3+} states. For Co/ZSM-5/W, the oxidation state of the cobalt is Co^{2+}, independent of whether the catalyst is calcined or reduced. In addition, the position and intensities of the Co $2p_{3/2}$ peaks for reduced 1.4% Co/ZSM-5/W suggests that nearly 80% of the cobalt is in a highly oxidized environment. The ISS data in Figure 1 shows the intensity ratio, Co/Si, typical of these catalysts.

The IR, XPS, and ISS data suggest that a portion of the Fe or Co enters the channels of the ZSM-5. The I_B/I_L ratios in Table 1, and infrared data on the intensities of OH bands in the 3500 cm^{-1} to 3800 cm^{-1} region, suggest that ion exchange of metal ions for H^+ occurs during metal impregnation. Figure 2 shows a schematic representation of this ion exchange.

To calculate the amount of ion exchange that occurs during cobalt nitrate impregnation onto ZSM-5, the infrared data in Table 1 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. For purposes of the following calculation, the calcined ZSM-5 is assumed to contain maximum Brönsted acidity. In such a case and with $SiO_2/Al_2O_3 = 22$, the number of Brönsted 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.,

$$N = N_B = N_{Al} = 8 \tag{1}$$

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 Brönsted 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:

$$N' = N'_B + N'_L \tag{2}$$

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

From Table 1, the Brönsted-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 Brönsted acid sites in ZSM-5 is similar to that in mordenite, i.e., $\varepsilon L/\varepsilon B = 1.5$, and of assuming that $N'_B/N'_L = (\varepsilon L/\varepsilon B)\,\frac{I'_B}{I'_L}$, the ratio N'_B/N'_L becomes the following:

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

Combining Equations 2, 3, and 4 gives the number of Brönsted 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 Brönsted-to-Lewis acidity distribution. The resulting distribution is governed by a set of equations similar to those in Equations 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:

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

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

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 Equations 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 Brönsted 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 Equations 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 Equations 6 through 10, with Equation 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:

$$N''_{Co} = 1.54,\ N''_B = 1.44,\ N''_L = 4.82,\ \text{and}\ N''_L = 6.26\ \text{for}\ 2Py/Co^{2+}$$

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. Table 2 summarizes the results of these calculations.

The number of OH stretching modes in the IR region from 3200 cm^{-1} to 3800 cm^{-1} for samples which have been O_2 calcined and evacuated is generally two. This characteristic is shown in Figure 3. Chemisorbed pyridine elminates the band due to acidic OH at 3610 cm^{-1} but does not affect the band at 3720 cm^{-1}. However, larger exposures of pyridine, i.e., when physically adsorbed pyridine is present, causes a perturbation of the 3720 cm^{-1} band. A similar perturbation is also observed after adsorption of H_2O (Figure 3), He (Figure 4), and other gases such as N_2, O_2, H_2 and D_2. The general behavior of the OH bands during such adsorption is a weakening intensity at 3610 cm^{-1}, an increase in band intensity at 3680 cm^{-1}, followed by band formation and broadening at 3560 cm^{-1}, 2900 cm^{-1}, and 2480 cm^{-1}. Such changes suggest that the OH groups are easily perturbed by even inert gases such as He. These effects will be investigated further to elucidate their causes and to determine whether such factors influence catalytic activity.

TABLE 1. The ratio I_B/I_L after pyridine chemisorption on ZSM-5 supported catalysts

Catalyst	Pretreatment	I_B/I_L
ZSM-5	Calcined	1.74
ZSM-5	Reduced	1.74
2.8% Co/ZSM-5/AQ	Calcined	0.24
5.1% Co/ZSM-5/AQ	Calcined	0.27
1.4% Co/ZSM-5/W	Calcined	0.17
1.4% Co/ZSM-5/W	Reduced	0.22
3.8% Fe/ZSM-5/EX	Calcined	2.07
6.6% Co/ZSM-5/EX	Calcined	0.26
6.6% Co/ZSM-5/EX	Reduced	0.24

TABLE 2. **Calculation of Number of Acid Sites Per Unit Cell of ZSM-5 as obtained from IR. Studies of Chemisorbed Pyridine**

N : Total no., N_B : Brönsted,

N_L : Lewis, N_{Al} : Al sites,

N_{Co} : Co sites ($SiO_2/Al_2O_3 = 22$)

Sample	N $= N_B + N_L$	N_B	N_L $= N_{AL} + N_{Co}$	N_{Al}	N_{Co}	(NH_3)
H^+-ZSM-5	6.26	4.52	1.74	1.74	0.00	2.00
Co^{2+}-ZSM-5	4.57*	1.14	3.43	1.74	1.69	3.42

*Assuming 1 PY/Co^{2+}; $N = 6.26$ assuming 2 PY/Co^{2+}.

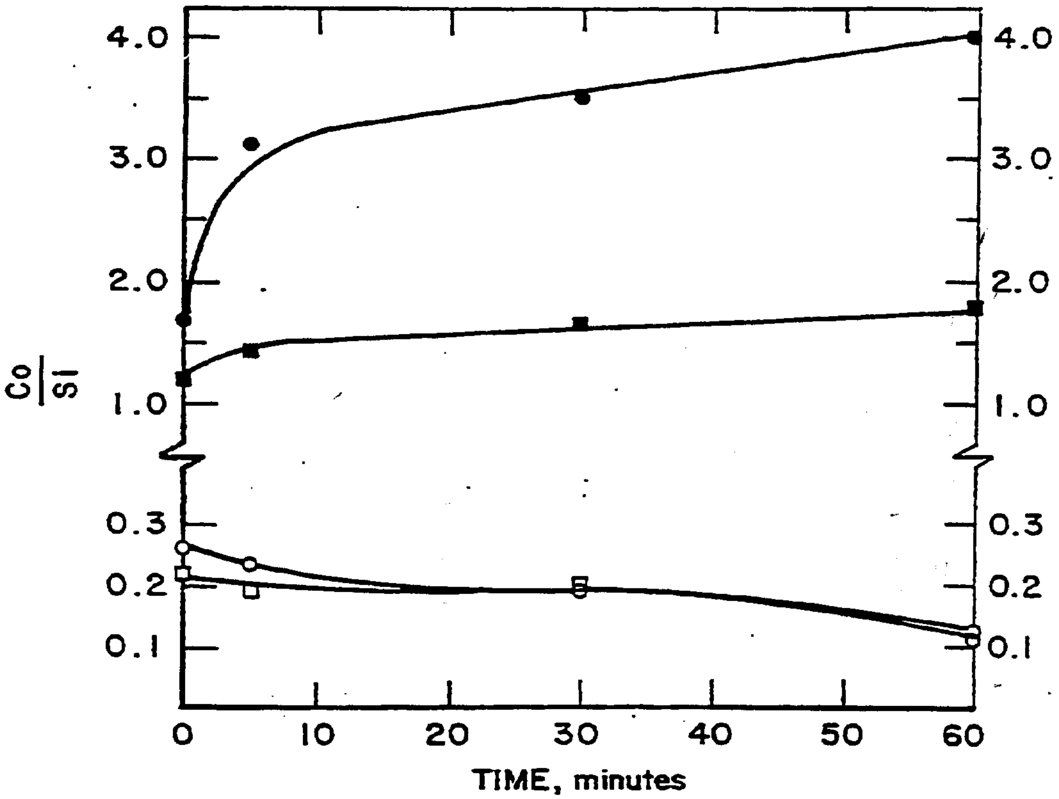

FIGURE 1. The Co/Si intensity ratios from ISS depth profiling studies of Co/ZSM-5. ●: 9% Co/ZSM-5, ■: 6% Co/ZSM-5, ○: 9% Co/ZSM-5-washed, □: 6% Co/ZSM-5 - washed.

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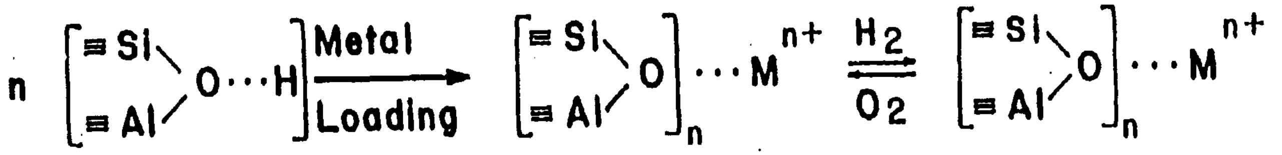
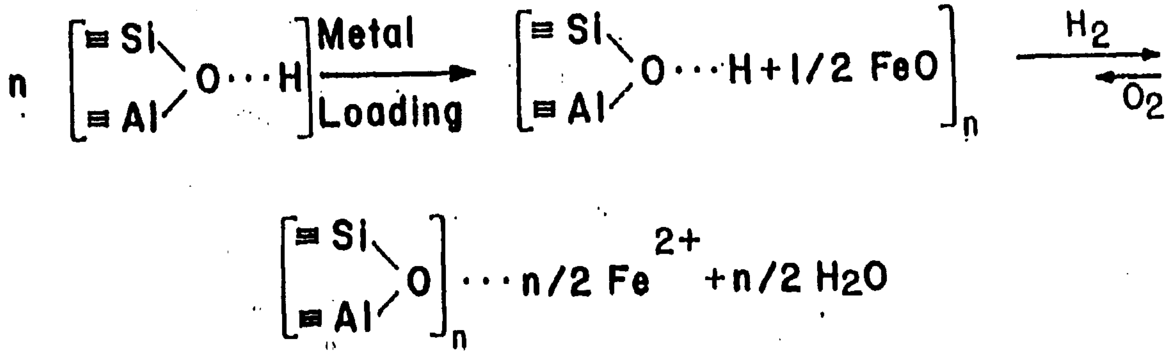
FIGURE 2. Infrared data shows that some cobalt and iron exists inside of ZSM-5 crystals.

a) $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and $Co_2(CO)_8$ gives



b) $Fe_3(CO)_{12}$ gives



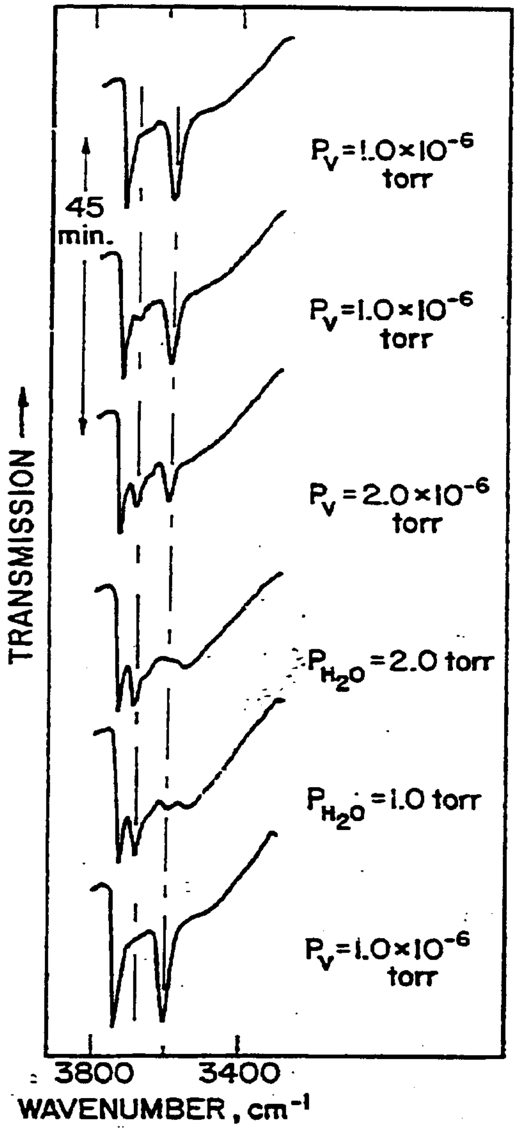


FIGURE 3. The effect of H_2O on the infrared spectra of acidic OH (3605 cm^{-1}) and other OH groups in ZSM-5; $SiO_2/Al_2O_3 = 70$.

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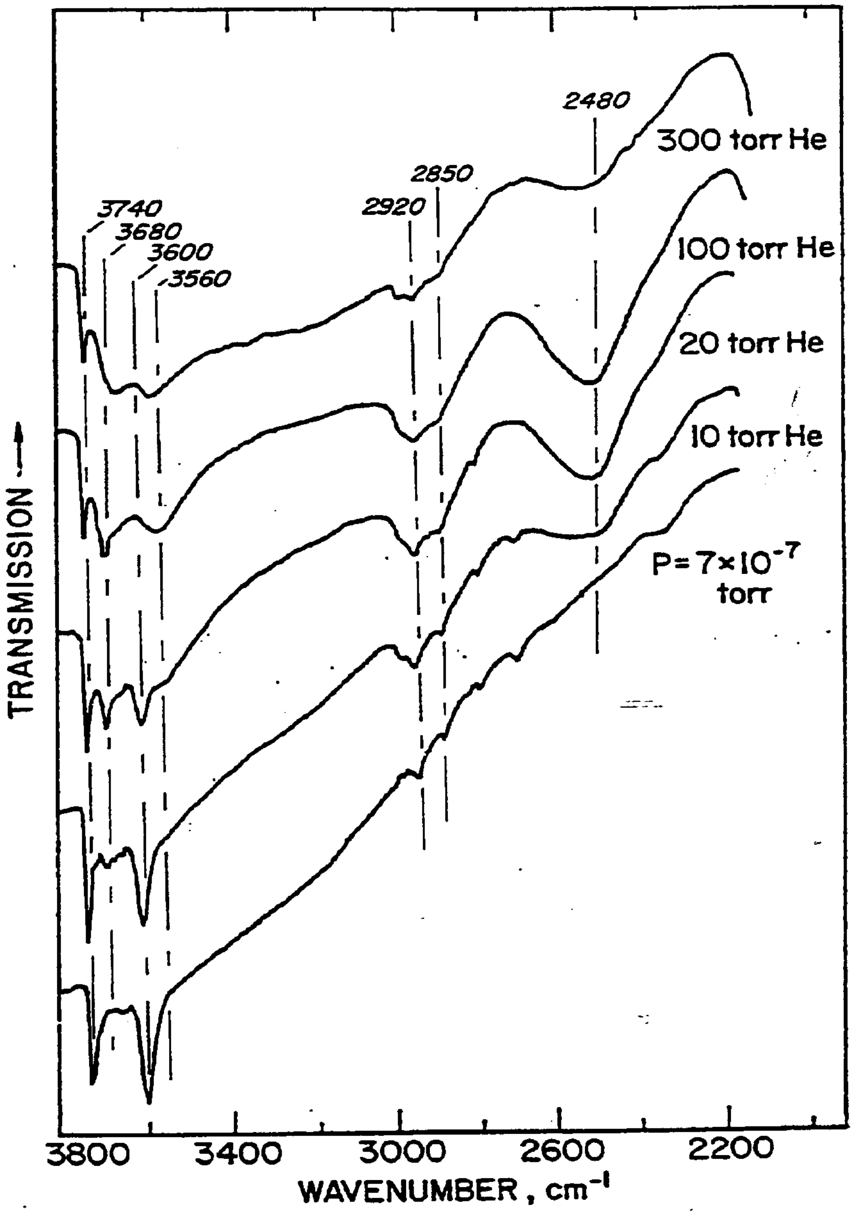

FIGURE 4 **Effect of He on the infrared spectra of the OH groups in ZSM-5; $SiO_2/Al_2O_3 = 70$.**

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