Report 6

METAL SPECIATION IN Fe/ZSM-5 AND Co/ZSM-5 RELATING TO SYNTHESIS GAS AND ETHYLENE CONVERSION

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1. To study the effect of impregnation of transition metals, Co and Fe, on the surface acidity of ZSM-5.

2. To determine the nature, strength and distribution of acid sites on M/ZSM-5 catalysts.

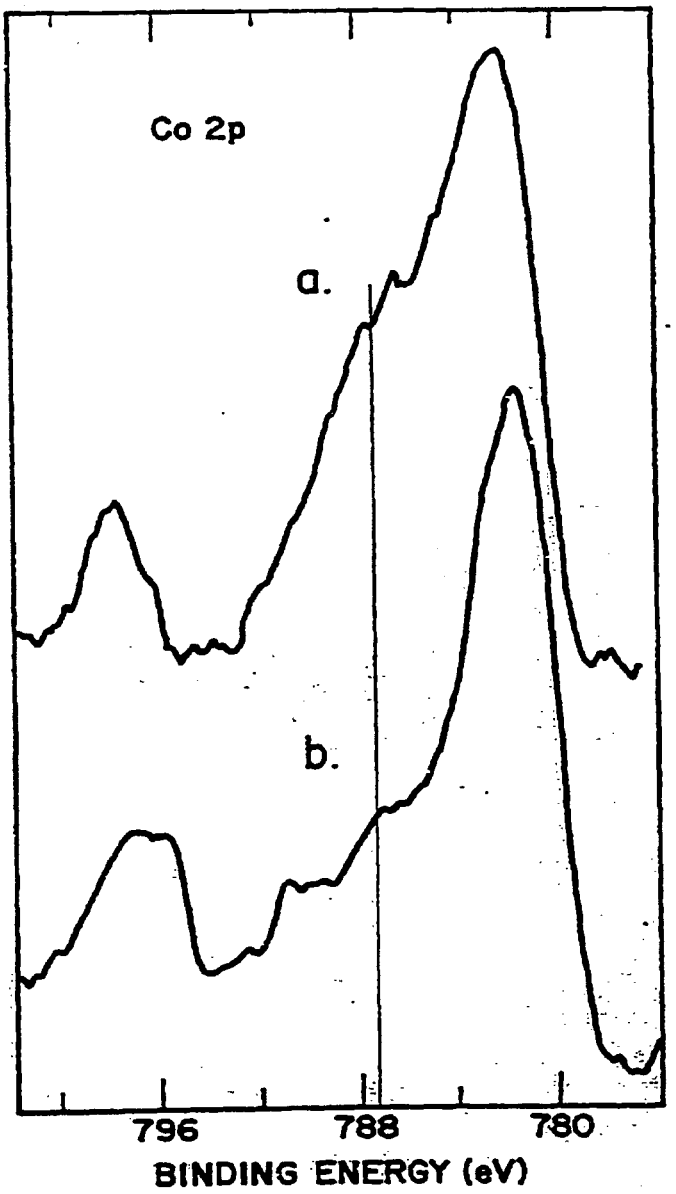
3. To find correlations between surface acidity and the Syn-gas conversion activity.

BSI/1006

FT - Synthesis Using Metal/ZSM-5 Catalysts

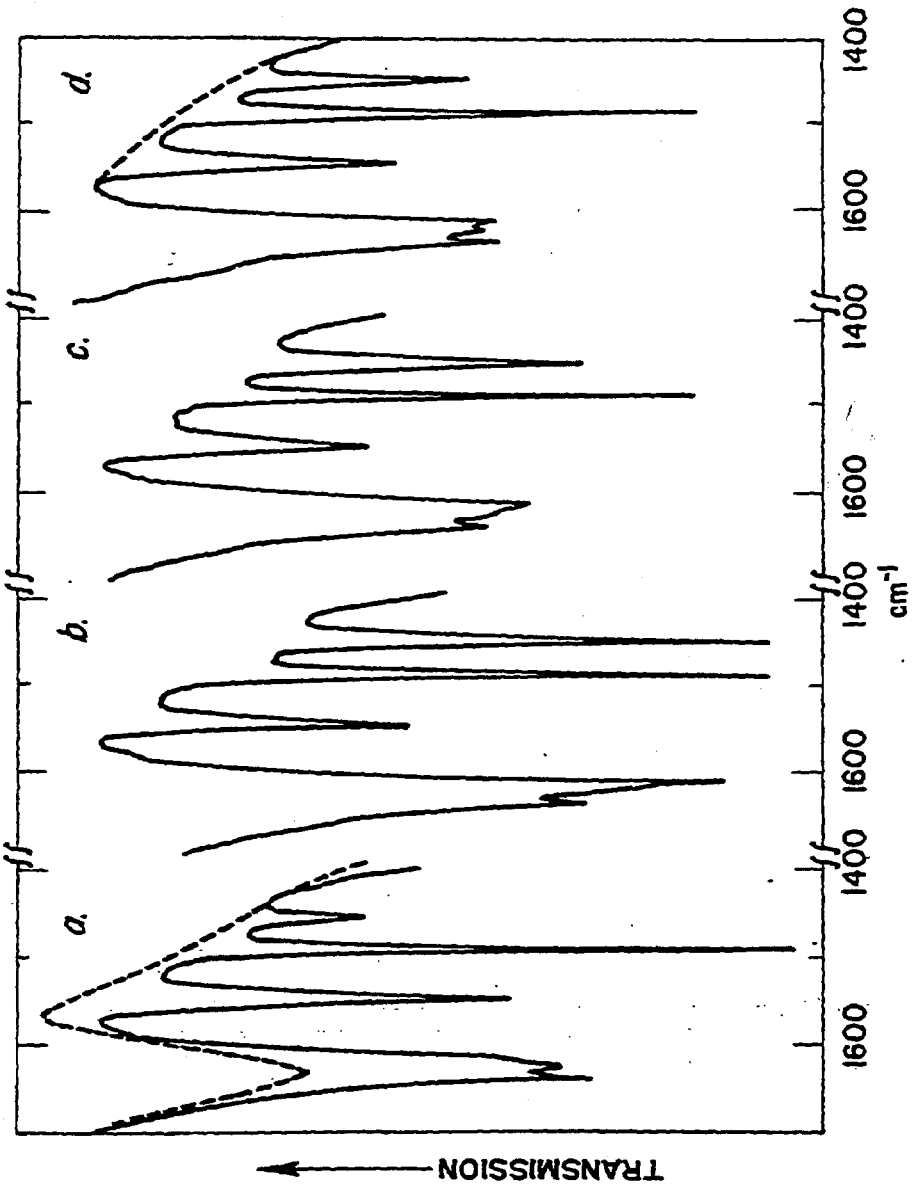
$CO + H_2$ → Metal Function → Paraffins, Olefins, Oxygenates

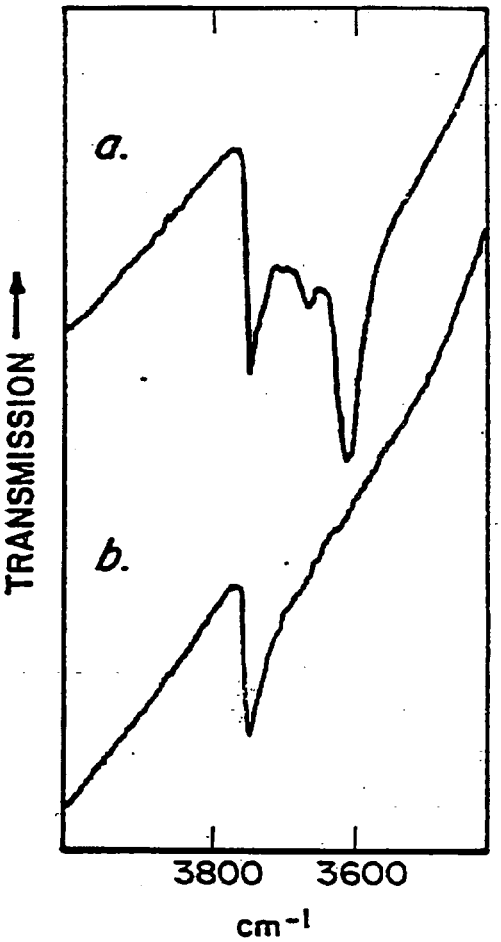
→ Zeolite Function → Aromatics, Branched Hydrocarbons



The XPS spectra of Co 2p peaks for 6% Co/ZSM-5 in (a) as-synthesized and (b) 150°C calcined forms.

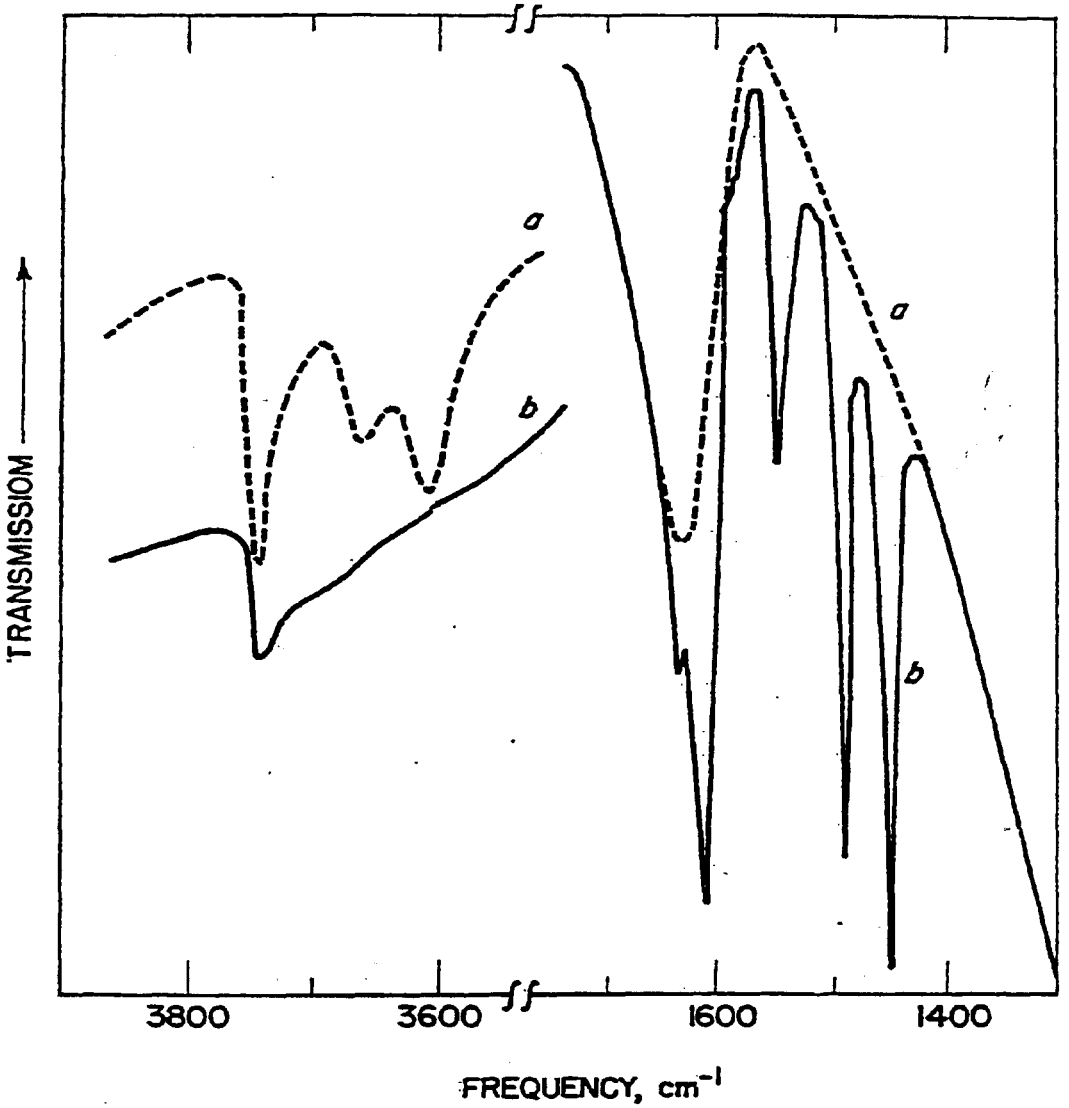
BSI/1254


d.
c.
b.
a.
1600
1400
1600
1400
1600
1400
1600
cm⁻¹
TRANSMISSION



The OH bands for 7.1% Fe/ZSM-5, $Fe_3(CO)_{12}$ impregnation, after 450°C calcination degassing *(a.)*, and after pyridine exposure and evacuation at 150°C *(b.)*.

BSI/603

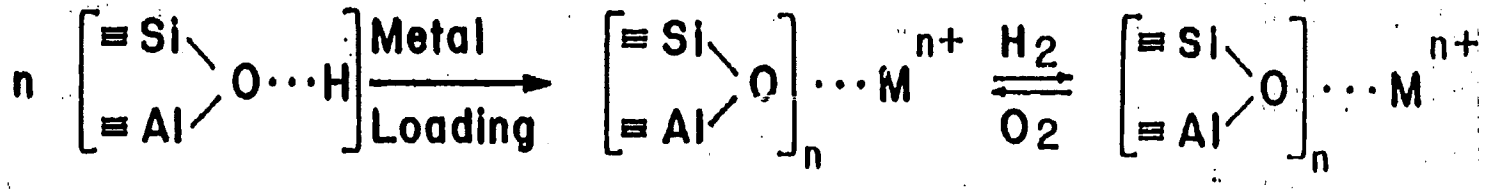

TRANSMISSIOM
a
b
a
b
3800
3600
1600
1400
FREQUENCY, cm⁻¹

Catalysts	Prepn.	Pretreatment	Brönsted Band	Lewis Band	1490 cm^{-1} Band	I_B/I_L
3% Fe/ZSM-5	PM	Calcined	1546	1447	1491	1.30
3% Fe/ZSM-5	AQ	Calcined	1549	1452	1492	0.72
3% Fe/ZSM-5	CO	Calcined	1548	1450	1492	2.07
7% Fe/ZSM-5	CO	Calcined	1548	1455	1495	3.30
7% Fe/ZSM-5	CO	Reduced	1547	1449	1491	0.28

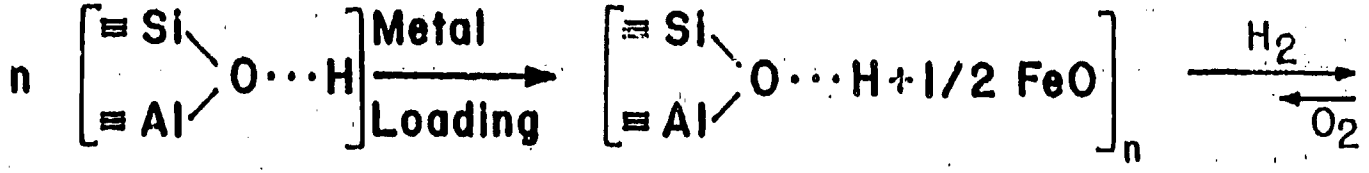
Catalysts	Prepn.	Pretreatment	Brönsted Band	Lewis Band	1490 cm^{-1} Band	I_B/I_L
3% Co/ZSM-5	AQ	Calcined	1548	1453	1492	0.24
3% Co/ZSM-5	AC	Calcined	1545	1450	1490	0.29
3% Co/ZSM-5	CO	Calcined	1548	1452	1493	0.38
6% Co/ZSM-5	AQ	Calcined	1545	1450	1492	0.27
6% Co/ZSM-5	AC	Calcined	1545	1450	1492	0.14
6% Co/ZSM-5	CO	Calcined	1547	1452	1493	0.26
6% Co/ZSM-5	CO	Reduced	1547	1452	1492	0.24
6% Co/ZSM-5-Washed	AQ	Calcined	1548	1450	1492	0.17
6% Co/ZSM-5-Washed	AQ	Reduced	1548	1450	1491	0.22
0.8% Co/ZSM-5	IX	Calcined	1548	1452	1491	0.97

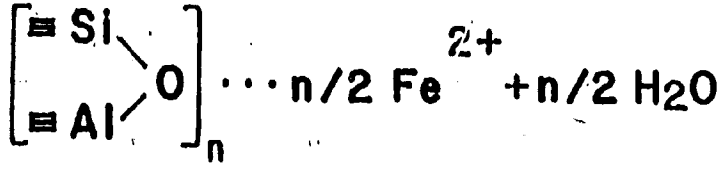
Infrared data shows that some cobalt and iron exists inside of ZSM-5 crystals.

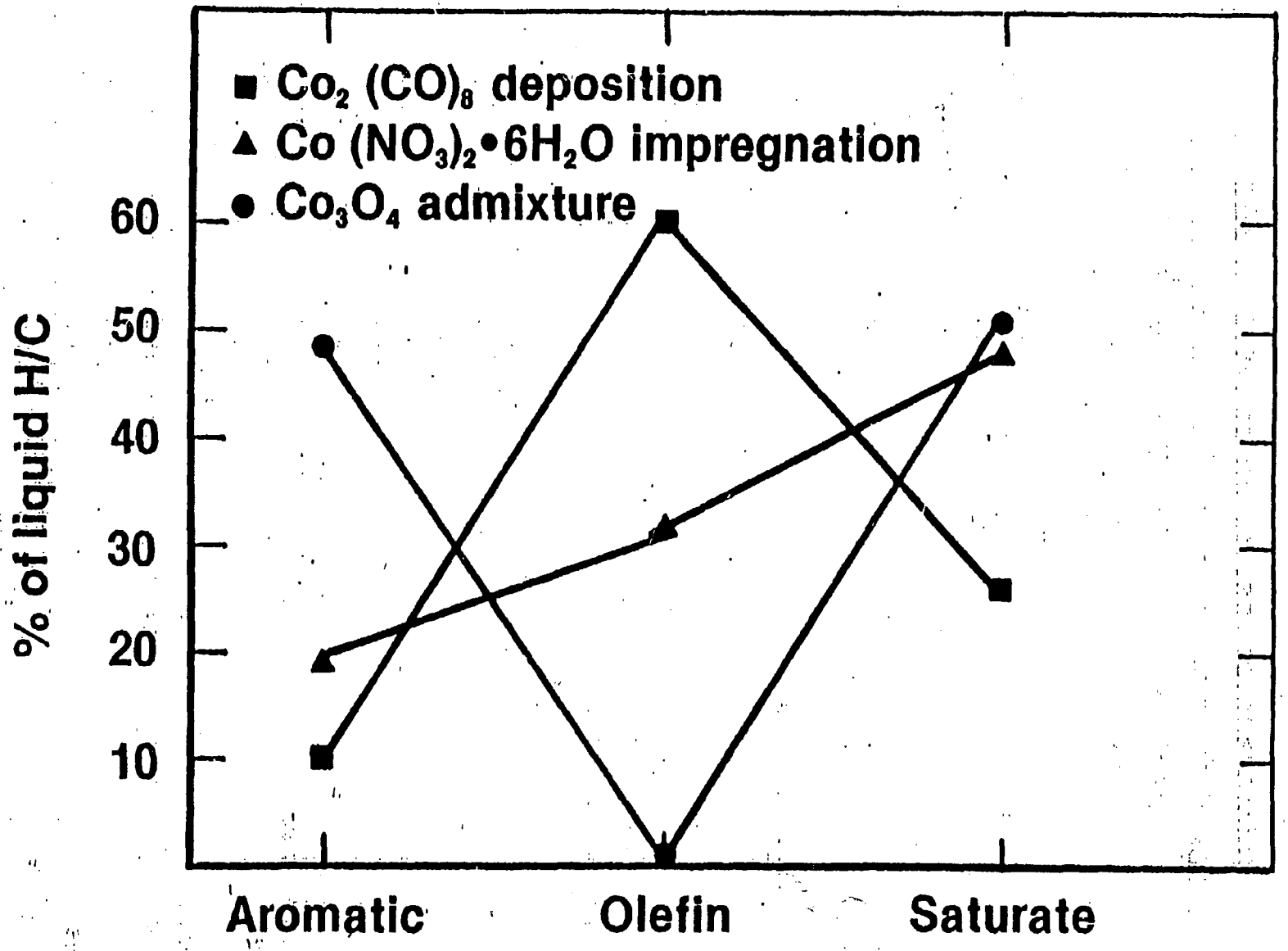
a) $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and $Co_2(CO)_8$ gives



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







1:1 Synthesis Gas Conversion over Co/ZSM-5, 280°C

Microreactor results on conversion and product distribution from Co/ZSM-5 catalysts. $H_2/CO = 1$; P = 21 ATM, T = 280°C Feed Rate, GHSV = 1000 hr^{-1}

	Co/ZSM-5-W	9% Co/ZSM-5 (Metal Nitrate impregnation	8.5% Co/ZSM-5 (Physical mixture)
CO Conversion	Trace	56.5	55.0
H_2 Conversion	Trace	85.8	66.5
Product Composition (wt%)			
CO_2	0	18.6	12.0
H_2O	0	46.1	51.3
CH_n	Trace	35.2	36.6
Composition of CH_n (wt%)			
CH_4	Trace	24.4	31.2
C_2H_4	0	0.0	0.0
C_2H_6	Trace	2.7	3.9
C_3H_6	0	0.8	0.0
C_3H_8	Trace	2.7	7.1
C_4H_8	0	0.8	0.0
C_4H_{10}	Trace	5.4	15.7
C_5^+ (Not Wax)	Trace	62.2	41.1
Wax	0	0.8	0.9
Liquid Product Composition (vol.%)			
Aromatics	*	19.5	48.5
Olefins	*	32.5	0.5
Saturates	*	48.0	51.0

*Quantity too small for FIA analysis.

1. ZSM-5 IS AN ACIDIC SUBSTANCE POSSESSING BOTH BRÖNSTED AND LEWIS ACID CENTERS.

2. SOURCE OF BRÖNSTED ACIDITY IS SURFACE OH GROUPS. INFRARED BANDS OF THESE GROUPS ARE LOCATED AT 3610 CM^{-1} AND 3680 CM^{-1}.

3. IN METAL LOADED ZSM-5, TWO SITES ACT AS LEWIS ACID CENTERS:

   A. TRI-COORDINATED, STRUCTURAL ALUMINUM

   B. METAL IONS AT EXCHANGED SITES

4. IMPREGNATION OF METAL NITRATE SOLUTIONS ONTO ZSM-5 PRODUCES TWO METAL-CONTAINING SPECIES.

   A. METAL OXIDE CRYSTALITES ON THE EXTERNAL SURFACE OF ZSM-5 CRYSTALLITES.

   B. METAL IONS INTERIOR TO ZSM-5 CRYSTALLITES RESULTING FROM ION EXCHANGE.

5. AMOUNT OF ION EXCHANGE IS DEPENDENT ON CONCENTRATION OF METAL.

6. Co/ZSM-5, CO CATALYSTS SHOW TWO METAL-CONTAINING SPECIES SIMILAR TO Co/ZSM-5, AQ CATALYSTS. HOWEVER, Fe/ZSM-5, CO CATALYSTS HAS AN ACIDITY DISTRIBTUION VERY DIFFERENT FROM OTHER ZSM-5 CATALYSTS.

7. A DECREASE IN CONCENTRATION OF AROMATICS DURING 1:1 SYNTHESIS GAS CONVERSION AT 280-300° CORRELATES WITH DEGREE OF ION-EXCHANGING.