Report 5

Syngas Conversion to Gasoline Range Hydrocarbons Using Metal-Zeolite Catalysts

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$$CO + H_2 \xrightarrow[\text{+ GR VIII METALS}]{\text{ZEOLITES}} \text{AROMATICS AND BRANCHED HYDROCARBONS}$$

ZEOLITES SUCH AS ZSM-5 PROVIDE SELECTIVE ROUTES TO GASOLINE RANGE HYDROCARBONS OWING TO THEIR SIZE AND SHAPE SELECTIVE PROPERTIES, AND THEIR STABILITY TO STEAMING.

MECHANISMS TO BE EXPLORED BY US ARE ILLUSTRATED BY THE FOLLOWING:

$$CO + H_2 \xrightarrow[\text{FUNCTION}]{\text{METAL}} \left[CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \right]$$

$$\xrightarrow[\text{FUNCTION}]{\text{ZEOLITE}}$$

C_6H_6, ETC.

BOTH FUNCTIONS CAN BE ACCOMPLISHED ON A SINGLE CATALYST SUCH AS A ZEOLITE IMPREGNATED WITH GROUP VIII ELEMENTS.

REFERENCES

1. Chang, C. D., Lang, W. M., and Silvestri, A. J., J. Catal. 56, 268 (1979).
2. Caesar, P. D., Brennan, J. A., Garwood, W. E., and Ciric, J., J. Catal. 56, 274 (1979).
3. Rao, V. U. S., Gormley, R. J., Pennline, H. W., Schneider, L. C., and Obermyer, R. T., Preprints, ACS Fuel Chemistry Division Symposium, 25, 119 (1980).
4. Rao, V. U. S., and Gormley, R. J., Hydrocarbon Processing, 59 (11), 139 (1980).

Structure of synthetic zeolite ZSM-5

(Reprinted from Nature, Vol. 272, No. 5652, pp. 437—438, March 30, 1978)

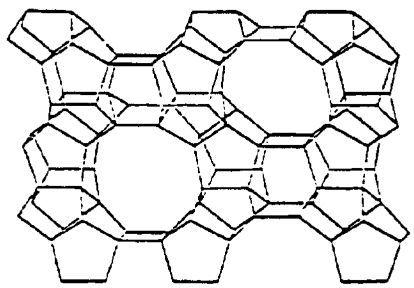


Fig. 3 Skeletal diagram of the (100)-face of the ZSM-5 unit cell. The y-axis is horizontal and the z-axis is vertical. Oxygen atoms are not shown. The nearly circular 10-membered ring apertures shown are the entrances to the sinusoidal channels which run parallel to [100].

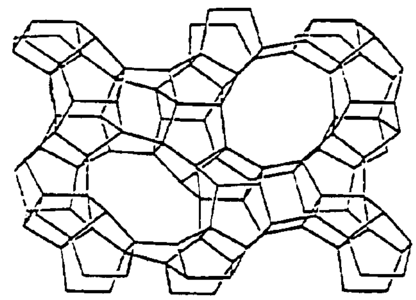


Fig. 2 Skeletal diagram of the (010)-face of the ZSM-5 unit cell. The x-axis is horizontal and the z-axis vertical. Oxygen atoms are not shown. The 10-membered ring apertures shown are the entrances to the straight channels which run parallel to [010].

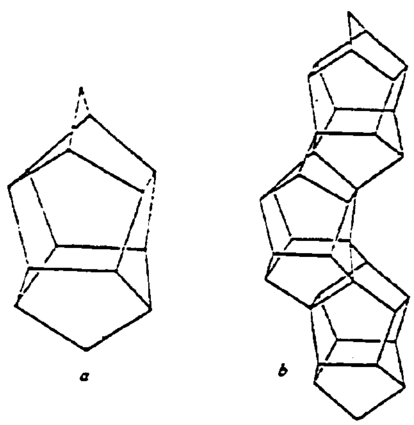


Fig. 1 Characteristic configuration (*a*) and its linkage within chains (*b*) in ZSM-5. These chains run parallel to [001]. Only T-atoms (Si, Al) are shown.

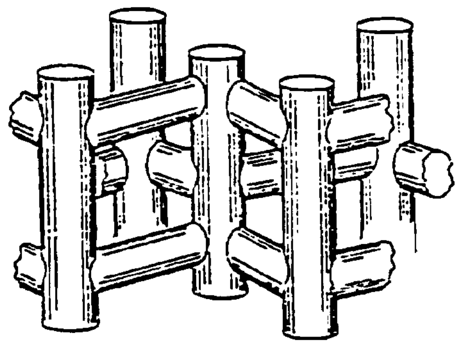
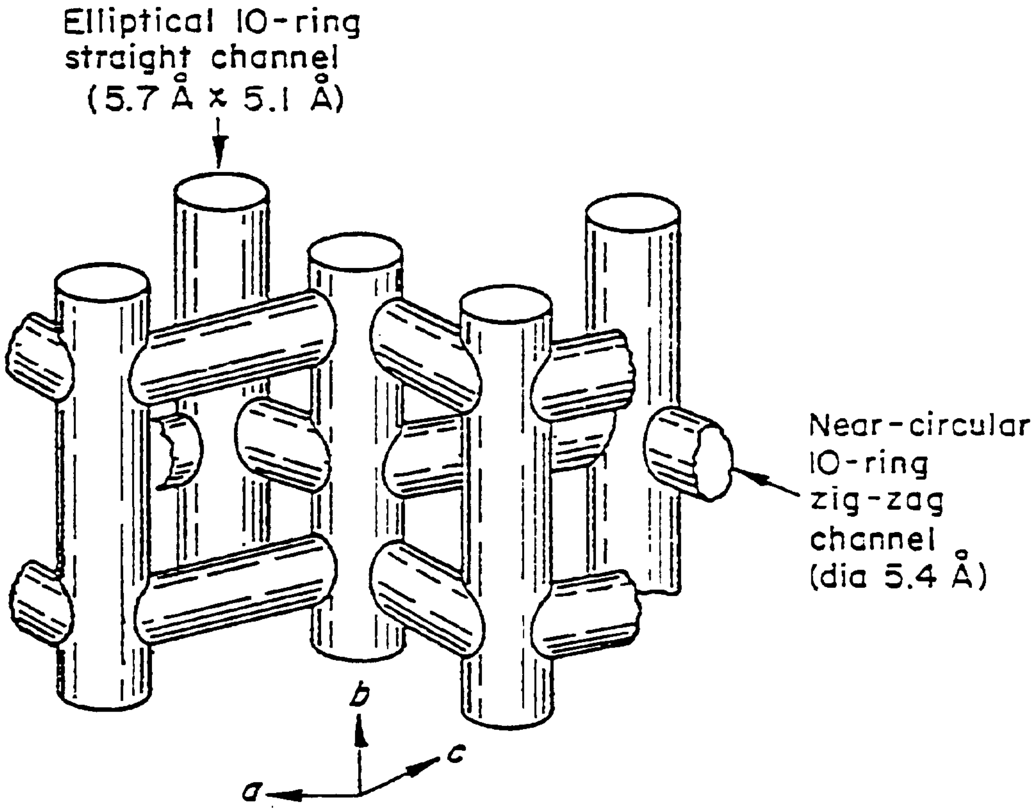


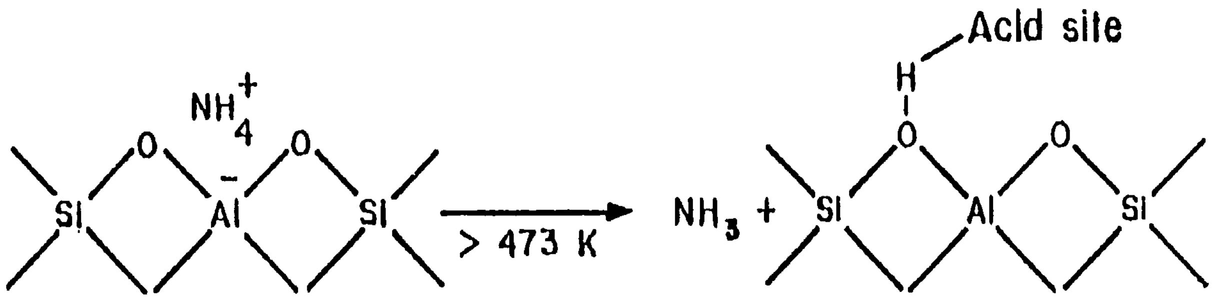
Fig. 4 The channel structure in ZSM-5.



Possible model of the pore structure of ZSM-5 and silicalite.

3-4-80 L-17436

Acidity of Zeolites



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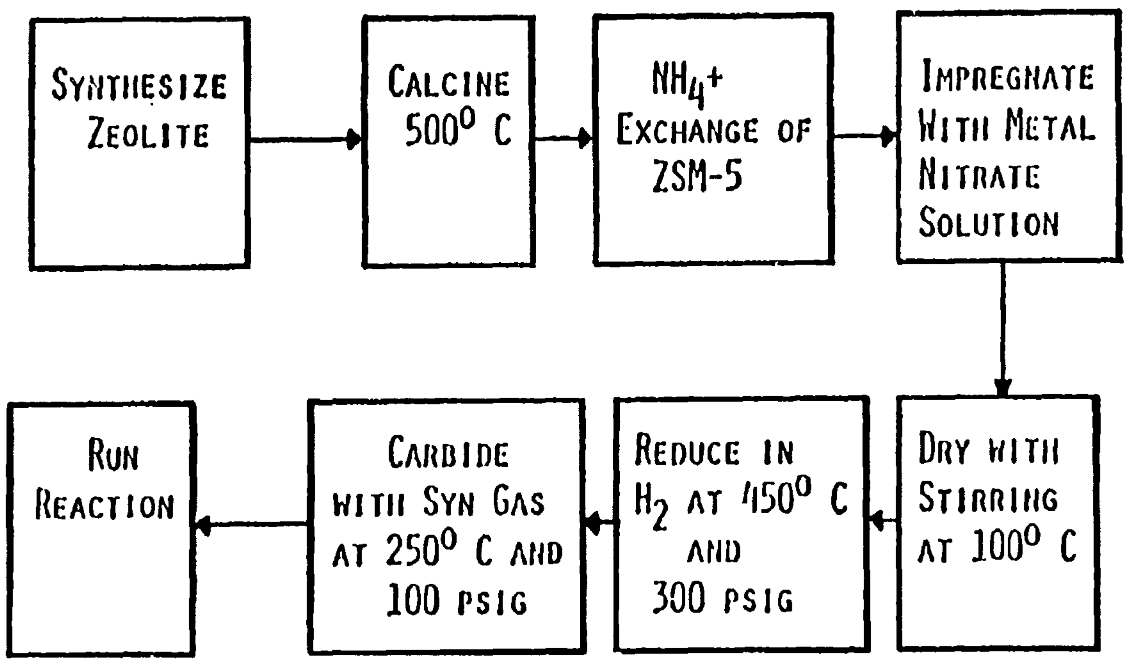
Preparation of Bifunctional Catalysts



BERTY REACTOR, $H_2/CO=2$, P=300 PSIG,
T=280°C, GHSV~1400

CATALYST	ZSM-5 (14.1% FE)	SILICALITE (13.6% FE)
CO CONVERSION %	50.8	39.4
H_2 CONVERSION %	33.0	16.5
LIQUID PRODUCT CHARACTERISTICS		
AROMATICS %	33	4
OLEFINS %	34	41
SATURATES %	31	33
OXYGENATES %	2	22
% GASOLINE (BP< 204°C)	92	77
RESEARCH OCTANE NO.	88.3	36.0

COMPOSITION OF OLEFINS IN C_5^+

Catalyst	Functional group (wt %)		
	1 olefin	2 olefin	Br-1-olefin
ZSM-5(Fe)	1.3	3.2	1.3
ZSM-5(Co)	1.6	10.9	1.9
Silicalite(Fe)	15.4	1.3	0.0

RESULTS OBTAINED BY D.-H. FINSETH, PETC

L-81412

BERTY REACTOR, $H_2/CO=1$, 300 PSIG, 280°C, 1000 HR^{-1}

CATALYST (ZSM-5 +)	(14.1% FE)	(5.4% FE, 1.3% CO)	(5.6% FE, 4.5% CO)	(9.0% CO)
CO CONVERSION %	61.5	23.1	30.8	53.5
H_2 CONVERSION %	40.1	38.8	46.5	87.2
LIQUID PRODUCT CHARACTERISTICS				
AROMATICS %	18	23	5	1
OLEFINS %	67	37	51	66
SATURATES %	13	28	38	30
OXYGENATES %	2	12	6	3
RESEARCH OCTANE NO.	87.0	90.3	72.7	57.8

CATALYST: ZSM-5 (10.3% Co)

IMPREGNATED USING SOLUTION OF COBALT NITRATE IN WATER OR ACETONE

PROCESS CONDITIONS: $H_2/CO = 1$, P = 300 PSIG

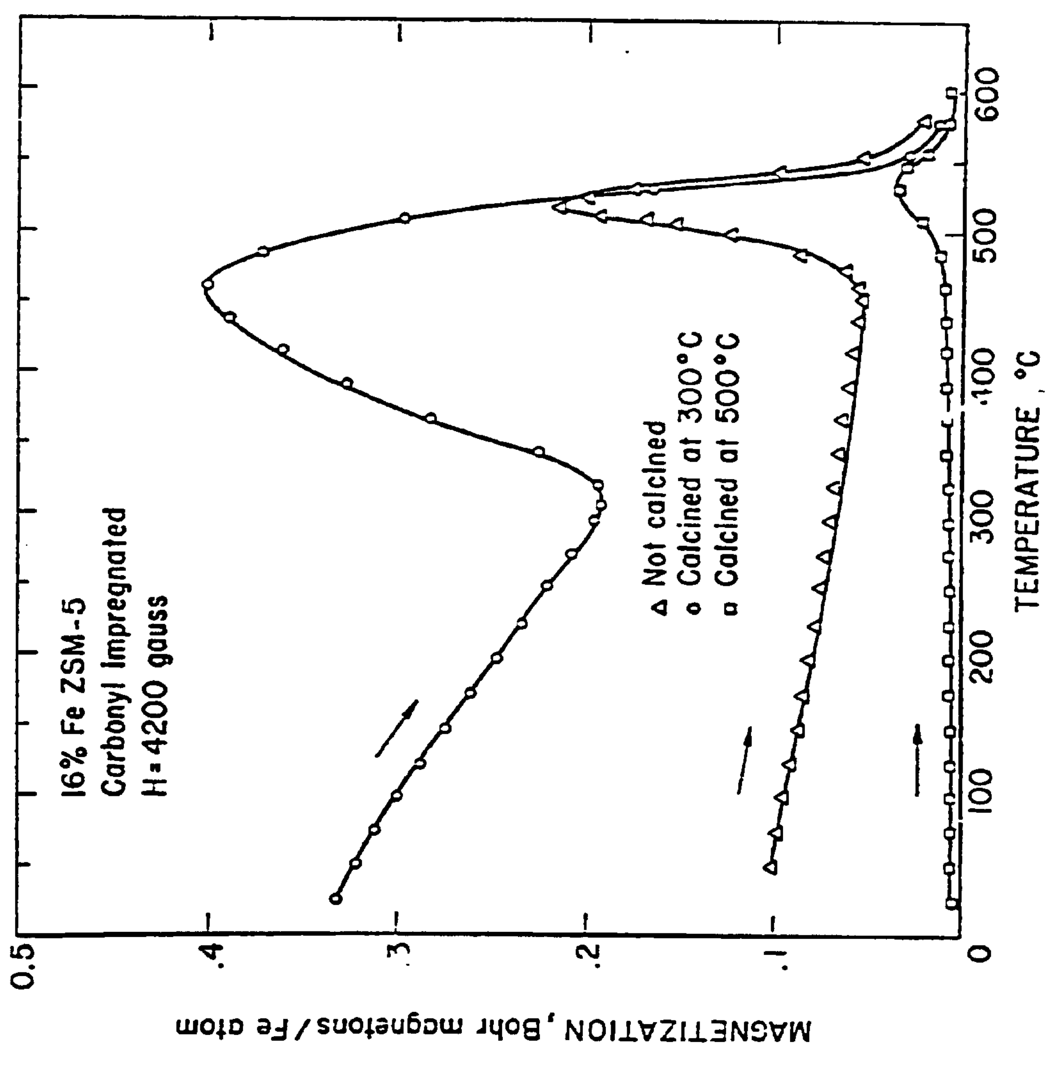
	WATER SOL.		ACETONE SOL.	
TEMPERATURE	280	300	280	300
CO CONVERSION %	47.6	56.2	39.4	40.7
H_2 CONVERSION %	92.5	94.4	83.1	90.2
CH_N IN TOTAL PROD (WT.%)	36.5	32.8	39.9	39.9
HYDROCARBON PRODUCT DIST. (WT.%)				
$C_1 - C_4$	52.8	81.7	48.9	80.7
C_5 + (LIQUID)	47.2	18.3	51.1	19.3
LIQUID HYDROCARBON PROPERTIES:				
AROMATICS %	5.0	14.0	7.0	49.0
OLEFINS %	54.0	61.5	37.0	36.0
SATURATES %	41.0	24.5	56.0	15.0

Table 1. Product Distribution From Syngas Conversion Using ZSM-5 (10.4 wt % Co) Catalyst *

Feed Gas: $H_2/CO = 1$, P = 300 psig

Temperature (^{o}C)	280	280	300
Flow Rate (GHSVO)	1000	500	500
CO Conversion (%)	38.1	35.8	51.0
H_2 Conversion (%)	85.0	85.1	90.9
Hydrocarbon Product Distribution (%)			
$C_1 - C_4$	55.4	63.3	80.4
C_5+ (Liquid)	44.6	36.7	19.6
Liquid Hydrocarbon Composition (%)			
Aromatics	7.5	17.0	33.5
Olefins	53.0	50.5	38.0
Saturates	39.5	32.5	28.5

*Co impregnated using the nitrate solution in acetone



MAGNETIZATION STUDIES BY R. T. OBERMYER,
PENN. STATE UNIVERSITY, McKEESPORT

Table 2. Conversion and Selectivity to Liquid Hydrocarbon Products of Two ZSM-5 (Fe) Catalysts Prepared by Different Methods, as a Function of Time on Stream.

Feed Gas: $H_2/CO = 1$, P = 300 psig,

Flow Rate (GHSV) = 1000 hr

Cumulative Time (Hrs)		0-48	48-96	96-168
ZSM-5 (16% Fe) Fe impregnated using $Fe_3(CO)_{12}$	CO conv %	54.6	54.1	55.3
	H_2 conv %	64.9	64.4	64.5
	Liquid CH_N%	49.9	47.1	46.6
ZSM-5 (14.5% Fe) Fe impregnated via precipitated catalyst	CO conv %	76.0	69.9	71.9
	H_2 conv %	66.4	71.2	73.0
	Liquid CH_N%	30.6	18.0	14.2

*Catalyst prepared by Janet E. Crawford and Gordon A. Melson, Department of Chemistry, Virginia Commonwealth University, Richmond

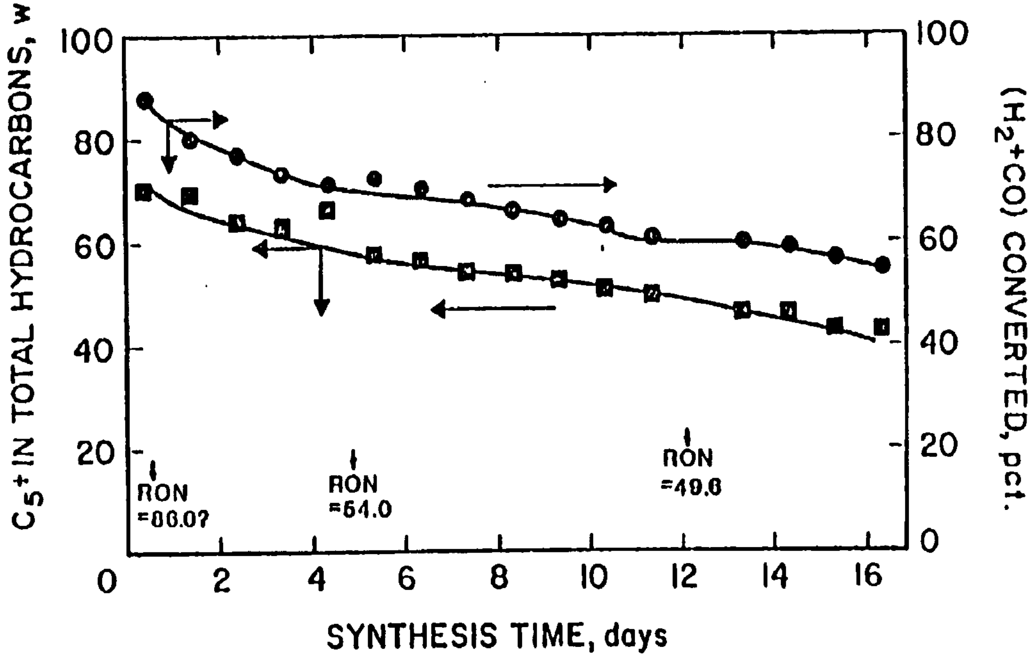
PROMOTER ACTION OF THORIUM

BERTY REACTOR, $H_2/CO=1$, 300 PSIG, 1000 HR^{-1}

CATALYST (ZSM-5 +)	(6.8% CO)		(10.2% CO, 1.5% TH)	
TEMP °C	260	280	260	280
CO CONVERSION %	28.3	30.0	35.5	78.3
H_2 CONVERSION %	52.7	59.6	88.1	92.4
LIQUID CH_N %	58.1	34.4	67.1	58.2
LIQUID HYDROCARBON CHARACTERISTICS				
AROMATICS %	5.0	4.5	1.5	3.0
OLEFINS %	23.5	21.5	83.0	68.0
PARAFFINS %	71.5	74.0	15.5	29.0
RESEARCH OCTANE NO.	37.7	59.9	62.1	86.0

Catalyst	PETC Catalyst ZSM-5 (Co, ThO_2)		Mobil Catalyst ZSM-5 + ThO_2
H_2/CO in feed	1.0	1.0	1.0
Pressure (PSIG)	300	300	1200
Temperature °C	280.0	279.0	426.7
CO conversion %	78.3	82.2	22.4
H_2 conversion %	92.4	94.4	15.2
Hydrocarbon Product Distribution:			
Methane	28.2	19.8	17.3
C_2 - C_4 hydrocarbons	10.8	10.6	73.8
C_5^+ (Liquid)	61.0	69.6	8.9
Aromatics in C_5^+	3.0		41.6
Research Octane No.	86.0		

Catalyst: ZSM-5 (14% Co, 2.2% Th) T=280°
Feed: $H_2/CO=1$, P=300 PSIG, Flow rate (GHSV)=1000hr^{-1}



C-81-114

BERTY REACTOR. $H_2/CO=1$, 300 PSIG, 280°C, 1000 HR^{-1}

CATALYST	NU-1 (10.3% FE)		NU-1(10.3% FE) + H-MORDENITE	
TEMP°C	280	300	280	300
CO CONVERSION %	49.8	58.2	29.4	65.9
H_2 CONVERSION %	52.2	53.8	39.0	60.5
LIQUID PRODUCT CHARACTERISTICS				
AROMATICS %	3	3	6	5
OLEFINS %	78	71	68	74
SATURATES %	16	25	21	19
OXYGENATES %	2	1	5	2
RESEARCH OCTANE NO.	55.6	64.0	75.8	79.7

BERTY REACTOR RESULTS WITH CO-RICH SYNGAS

PROCESS CONDITIONS: H_2/CO=0.68, P=300 PSIG, T=280°C

CATALYST: 10.3% FE-NU-1 - .59(H-MORD).

CO CONVERSION %	48.0
H_2 CONVERSION %	58.6

<u>LIQUID PRODUCT CHARACTERISTICS</u>

AROMATICS %	10.
OLEFINS %	66
SATURATES %	15
OXYGENATES %	2
RESEARCH OCTANE NO.	78

CONCLUSIONS

(1) ZEOLITE ACIDITY PLAYS AN IMPORTANT ROLE IN THE FORMATION OF AROMATICS FROM SYNTHESIS GAS BY BIFUNCTIONAL CATALYSTS AS STRIKINGLY EVIDENCED IN A COMPARISON OF THE PRODUCT SLATES FROM ZSM-5 (14.1% FE) AND SILICALITE (13.6% FE).

(2) SILICALITE IMPREGNATED WITH FE AND PROMOTED WITH K HAS AN EXCEPTIONALLY HIGH SELECTIVITY FOR THE PRODUCTION OF C_2-C_4 OLEFINS FROM SYNTHESIS GAS.

(3) THE TRANSITION METAL COMPONENT IMPREGNATED INTO THE ZEOLITE PLAYS AN IMPORTANT ROLE IN SELECTIVITY AS SEEN FROM THE ZSM-5 (FE-CO). IN THIS CONTEXT, ZEOLITES CONTAINING BIMETALLIC CLUSTERS ARE OF SPECIAL INTEREST.

(4) MEDIUM PORE ZEOLITE NU-1 APPEARS TO BE A PROMISING SUPPORT WITH SHAPE SELECTIVE AND MODERATELY ACIDIC PROPERTIES. NU-1 (FE) YIELDS GASOLINE RANGE HYDROCARBONS WHOSE OCTANE NUMBER CAN BE INCREASED BY ADDITION C H-MORDENITE TO THE CATALYST.

(5) THORIUM HAS SIGNIFICANT PROMOTER ACTION WHEN ADDED TO ZSM-5(CO), CAUSING ENHANCEMENT OF LIQUID HYDROCARBON YIELD AND OCTANE RATING OF PRODUCT.

(6) THE CATALYST ZSM-5(CO) WAS FOUND TO YIELD A CONSIDERABLY HIGHER FRACTION OF AROMATICS (49%) WHEN COBALT WAS INTRODUCED IN AN ACETONE MEDIUM, IN COMPARISON TO THE FRACTION (12%) OBTAINED WHEN COBALT WAS INTRODUCED IN AN AQUEOUS MEDIUM. IN BOTH CASES, COBALT NITRATE WAS THE SALT USED FOR IMPREGNATION, AND THE REACTION WAS RUN AT 300°C.