

Report 2

**PARTICLE SYNTHESIS AND PROPERTIES OF ZEOLITE
CATALYSTS FOR SYNTHESIS GAS - GASOLINE CONVERSION**

**G. Dodwell
Worcester Polytechnic Institute**

Particle Synthesis and Properties of Zeolite
Catalysts for Synthesis Gas - Gasoline Conversion

Glenn W. Dodwell and L.B. Sand
Worcester Polytechnic Institute

This study was started about a year ago to contribute to the ongoing research effort at PETC in the preparation and evaluation of bifunctional ZSM-5 based Fischer Tropsch catalysts. The first objective of this program was to investigate the P, T, X, t parameters involved in the synthesis of ZSM-5 to delineate the conditions under which a wide variety of ZSM-5 type catalysts could be hydrothermally crystallized. Toward this end systems including TPA (tetrapropylammonium), Na; TPA; K; TPA, Na; TPA, NH₄; TPA, NH₄, Na; TPA, NH₄, K, TPA, NH₄, Li; TPA, NH₄, Na, Fe; with or without Al₂O₃, and all containing H₂O and SiO₂ were investigated. Depending on the system, uniformly sized ZSM-5 crystals were obtained over a widely variant size range from submicron to 180 micrometers exhibiting a number of different crystal morphologies. Recent examples of morphological variations evidenced in the TPA-NH₄ - SiO₂ - Al₂O₃ - H₂O system follow (plate 1 & 2). ZSM-5 varieties containing Si/Al₂O₃ ratios from 10 to 150 were also prepared in the TPA-Na-SiO₂-Al₂O₃-H₂O system at PETC in conjunction with the ORAU* summer program.

To evaluate the properties of these catalysts, an integrated computerized zeolite laboratory was designed and implemented. The heart of this laboratory is a custom 128K DEC PDP 11/23

*Oak Ridge Associated Universities

microcomputer containing a programmable real-time clock, 8 serial I/O lines (2-DLV11-J), a 7.8 megabyte firm disk and 2 megabyte floppy (DSD-880), an 8 channel differentially configured 16 bit resolution analog to digital converter (Data translation 2764-PGL), a 4 channel 12 bit resolution Digital to Analog Converter (DT-2700) and equipped with floating point, extended instruction set and a memory management unit.

The other main components of this research laboratory include Cahn electrobalance, a Philips X-ray powder diffractometer, a Chemical Data System (803) micropilot plant reactor, a P & E Sigma 1 B gas chromatograph, a Tektronix 4006-1 graphics terminal, a Tektronix 4662 Interactive Digital Plotter and a Texas Instrument Silent 700 terminal with cassette storage. The information transfer and plant control diagram is shown in figure 1.

Micro Pilot Plant

The micro pilot plant reactor system was designed to allow safe 24 hr operation of the tubular syn-gas reactor wherein the PDP 11/23 has dominion over the reactant feed, both space velocity and composition, the frequent reactant and product sampling and analysis by GC, and the responsibility for telephoning the appropriate personnel if the ambient CO con-

centration exceeds 50 ppm.

The feed control is accomplished by program control (D-A) of the voltage supplied 3 model 5850 Brooks constant mass flow controllers and the (A-D) monitoring of the voltage at the values. Computer power failure results in feed shut down and battery back up insures the distress telephone call is placed or replaced if number is busy. Reactor power failure results in the CDS failsafe shut down of the reactor. The ambient CO level is monitored by a General Electric digital CO detector and the analog output of this detector is followed by the 11/23 (A-D) to provide both concentration and dosage reporting.

The CDS reactor contains 3 solenoid operated valves for reactor bypass, product sampling, and feed sampling. The samples obtained are directed to the Sigma 1B heated sampling valve through a heated transfer line with a helium carrier. The GC sampling valve then directs the sample simultaneously to both an open tubular column (1 micro thick bonded phase methyl silicate DB1) and an OV101 pre column. When ethane eludes the pre column toward the carbosive S column, the valve is switched and the heavies in the pre column are vented. The two GC carriers then send the entire sample to the FID and the permanent gases H₂, CO, Ar, CO₂, H₂O, C₁ & C₂ to the HWD.

The product slate is then tabularized by the microprocessor in the Sigma 1B and sent to the 11/23 for storage through an

RS232-C interface. If the 11/23 is busy, the analysis report is stored on cassette tape by the Sigma.

The command to switch any of the four solenoid valves can be supplied by the CDS programmable timer, the PDP 11/23, or the Sigma 1B microprocessor. The two He carriers in the GC are under flow rate control of the program running in the Sigma 1B microprocessor as is the temperature program of the GC oven.

An overview of the reactor system is shown in Figure 1 and a tubing schematic excluding the feed control is shown in Figure 2.

Cahn Balance

The fourth channel of the D to A converter on the 11/23 is used to control the Cahn balance. The lowest four bits of the fourth D to A channel are sent to a 1 of 16 demultiplexer/decoder driver which commands the relay closures to operate the Cahn balance. Operations of the Cahn balance involves 3 solenoid valves, a sample position and a programmable oven.

Balance Operation

The first solenoid valve is opened to allow the rough down vacuum pump to evacuate the balance. The 11/23 then waits for the system to be evacuated and then turns on the programmable

oven to activate the sample. The first solenoid valve to the rough down pump is then closed and the second valve applies the high vacuum Hg diffusion vacuum balance and the third to the sorbate input section. After the activation period, the 11/23 shuts off the programmable oven and lowers the catalyst sample to the metallic base of the enclosure. This allows the sample to cool by conduction instead of radiation only. The third valve is then closed to isolate the balance from the gas input section and the operator is notified to introduce sorbate. The 11/23 then raises the sample and allows it to stabilize. Finally, the second valve is closed and the third valve is opened by the 11/23 which then measures catalyst weight and balance pressure 50 times/sec and balance temperature every 10 seconds. The pressure information is supplied to the 11/23 by a Baraton differential pressure transducer, the catalyst weight by the Cahn 1000 control unit and the temperature by a thermocouple (all analog). A schematic of the balance is shown in figure 3.

Preliminary Sorption Results

The balance system recently completed was utilized to evaluate the selectivity crossover for the adsorption of n-hexane and H₂O on ZSM-5 of varying SiO₂/Al₂O₃ ratios. Figures 4-10 depict the sorption rate curves for the aforementioned sorbates at 6.5 torr as a function of SiO₂/Al₂O₃

ratio. Table 1 shows the near equilibrium sorption capacities.

Discrete fast fourier transform of the 70,000 data points accumulated for each of these curves showed the sinusoidal noise oscillations present to be confined to a small frequency range. They can, therefore, be easily removed by reducing the intensity of the fourier coefficients in this frequency range and then doing the inverse transform. The sorbate surge in the initial part of the rate curve can be eliminated by running a non adsorbing blank with the same gas and pressure and then subtracting the two data sets. This is only possible by the timing synchronization made possible by computer control.

It is hoped that the speed and precision of this balance system will aid in the modeling efforts and diffusivity calculations.

The data work up is accomplished in the 11/23 in Fortran and the plotting is accomplished by a macro 11 assembly language graphics package written specifically for this system.

As programmed temperatures and weight can be measured the system can also be used as a TGA.

X-Ray Diffraction

The Philips XRD was interfaced with the 11/23 through a 60 MA Active to 20 MA passive converter followed by a 20 MA passive to RS232C converter (DLV11-KA) and connected to one of the 8 serial lines described. A fortran program was developed

to find locations in the (I,20) X-ray data where the decreasing slopes of the first derivative cross zero. These parts correspond to the peak maxima allowing the program to locate XRD peaks and report the corresponding line pattern in both tabular form (table 2) or in graphic form (figures 11-13). This capability aids in the identification of phases with extremely similar diffraction patterns such as ZSM-5 and ZSM-11.

Metal Impregnation

The synthesis of large crystals of ZSM-5 will aid in the determination of the extent of FT metal transport into the ZSM-5 lattice during various impregnation procedures and conditions. Preliminary work conducted with Dr. Rao at PETC seemed to indicate thoria migrated into silicalite and CO was excluded during an acetone impregnation of the nitrate salts. These large crystals were impregnated, sputtered with gold using a Sevac conductivac #1, fractured between two glass slides and observed with a ETEC autoscan SEM with a Princeton Gamma teck lithium drifted silicon detector. The absence of the gold peak helped to guarantee a spot under analysis was a fractured and not original surface. The fractured crystal surface shown in the lower right SEM of plate 3 shows the analysis spot positions labelled A to H. The analysis for each of these locations is shown in plate 4. The data appeared to indicate transport of thoria occurred into the silicalite pores where cobalt remained on the surface.

Conclusions

The exploratory synthesis work presented and that summarized in tables 5 to 7 contain recent work of Alfonso Nastro, Ryszard Mostowicz, Majid Ghamani and Hang Chi. ZSM-5 is unique in that it can be crystallized in a wide number of

different systems. The exploratory synthesis accomplished have provided recipes for the synthesis of ZSM-5 in particle sizes from submicron to 180 microns. The synthesis in the Na free TPA-NH₃ system eliminates the need for ion exchanging ZSM-5 to obtain the catalytically active hydrogen form.

The computerized zeolite laboratory is nearing completion and should expedite this coming year's research accomplishments.

Future Program

The synthesis of pentasyl zeolites in systems containing complexing agents and FT active transition agents might result in the occlusion of the transition metals during crystallization. Metals so occluded are likely to be well dispersed within the pore structure and might improve catalyst activity. Preliminary work in the Fe-silicalite system indicates that Fe is occluded and well dispersed in crystals which are large, particularly well formed and uniform in size. Future efforts will include attempting to prepare Fe-ZSM-5 and other bifunctional syn-gas catalysts by direct synthesis. Although the quantity of metal occluded might not, by itself be sufficient to promote good CO reduction behavior, well dispersed metal incorporated in this manner and supplemented by conventional metal impregnation techniques might enhance activity.

Plate 1

System: Quso - TPAOH

Composition:

4(TPA)₂O - 6(NH₄)₂O - Al₂O₃ -

59SiO₂ - 750 H₂O

Length of reaction: 48 hr

System: Quso - TPAOH

Composition:

10(TPA)₂O - Al₂O₃

59 SiO₂ - 750 H₂O

Length of reaction: 72 hr

The same sample of upper
right with magnification
10 times higher

System: Quso - TPAOH

Composition:

5(TPA)₂O - 5(NH₄)₂O

Al₂O₃ - 90 SiO₂ - 750 H₂O

Length of reaction: 3 hr

System: Quso - TPAOH

Composition:

5(TPA)₂O - 5(NH₄)₂O

90 SiO₂ - 750 H₂O

Length of reaction: 2h:20'

System: Quso - TPAOH

Composition:

4(TPA)₂O - 40 SiO₂ - 750

H₂O

Length of reaction: 8:40'

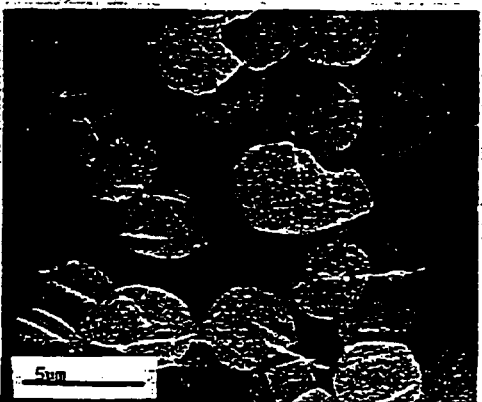
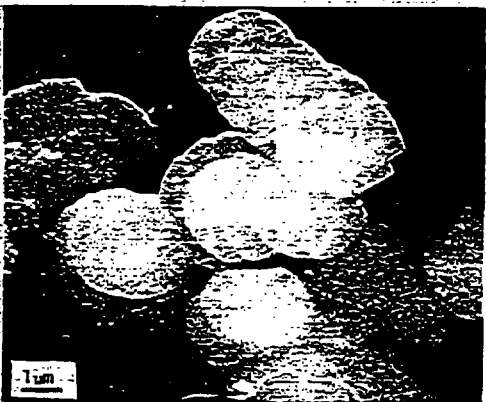
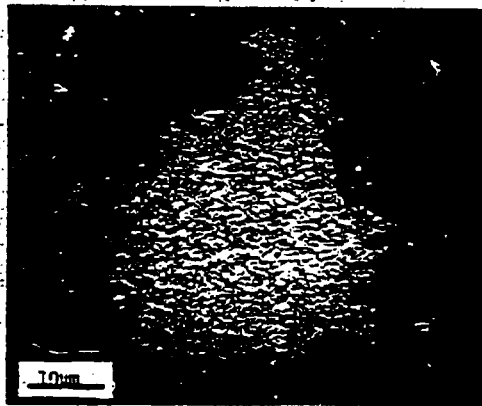


Plate 2

System: Ludox(AS40)
TPABr

Composition:
4(TPA)₂O - 60 (NH₄)₂O
Al₂O₃ - 59 SiO₂ - 750 H₂O
Length of reaction: 120 hr

System: Ludox (AS40)
TPABr

Composition:
4(TPA)₂O - 60 (NH₄)₂O
Al₂O₃ - 59 SiO₂ - 750 H₂O -
10 Cl NH₄
Length of reaction: 120 hr

System: Ludox(AS40)
TPABr

Composition:
4(TPA)₂O - 60 (NH₄)₂O
Al₂O₃ - 90 SiO₂ - 750 H₂O
Length of reaction: 123 hr

System: Ludox (AS40)
TPABr

Composition:
8(TPA)₂O - 60 (NH₄)₂O
Al₂O₃ - 90 SiO₂ - 750 H₂O
Length of reaction: 120 hr

System: Ludox(AS40)
TPABr

Composition:
4(TPA)₂O - 60 (NH₄)₂O
- 90 SiO₂ - 750 H₂O
(without Al₂O₃)
Length of reaction: 48 hr

The same sample on the
lower left with higher
magnification.

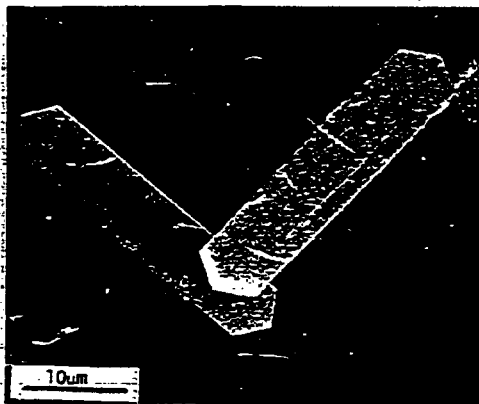
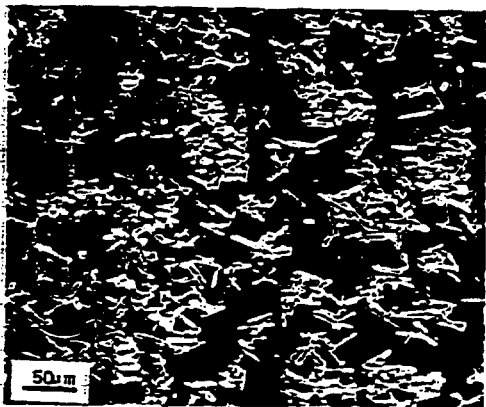
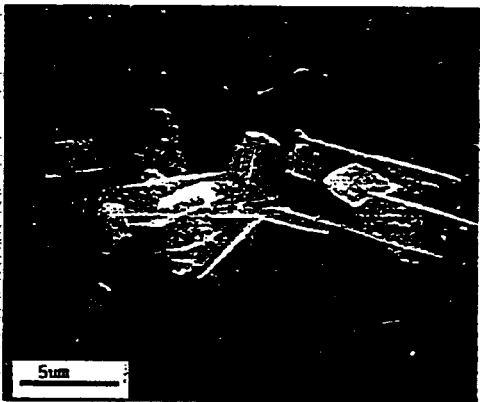
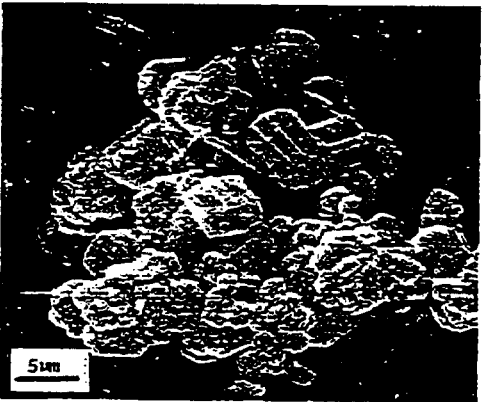
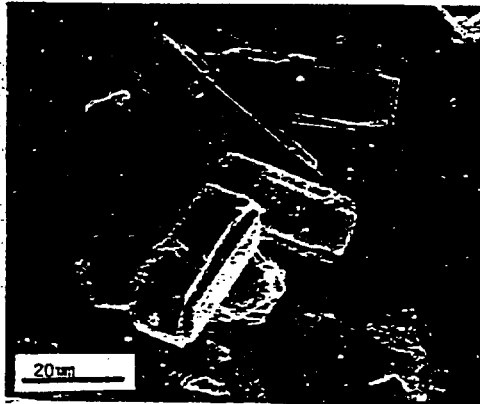
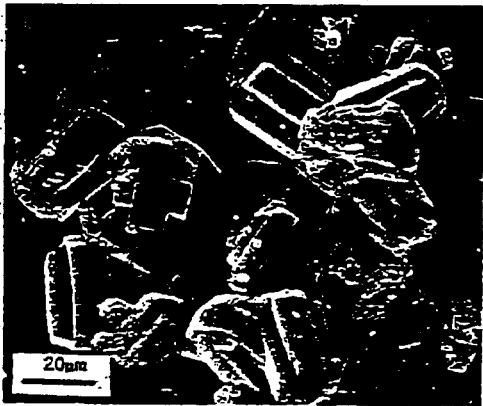
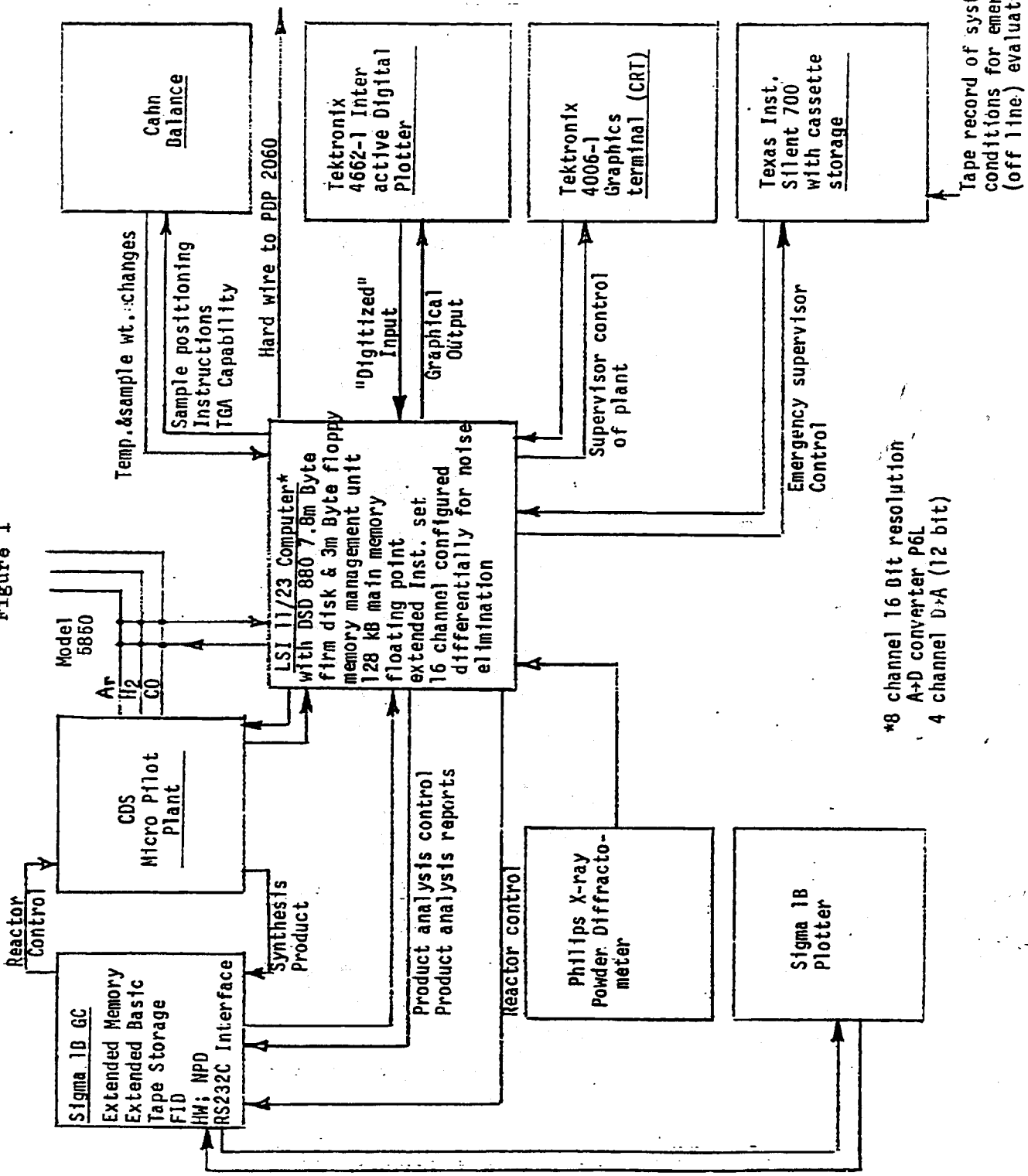


Figure 1

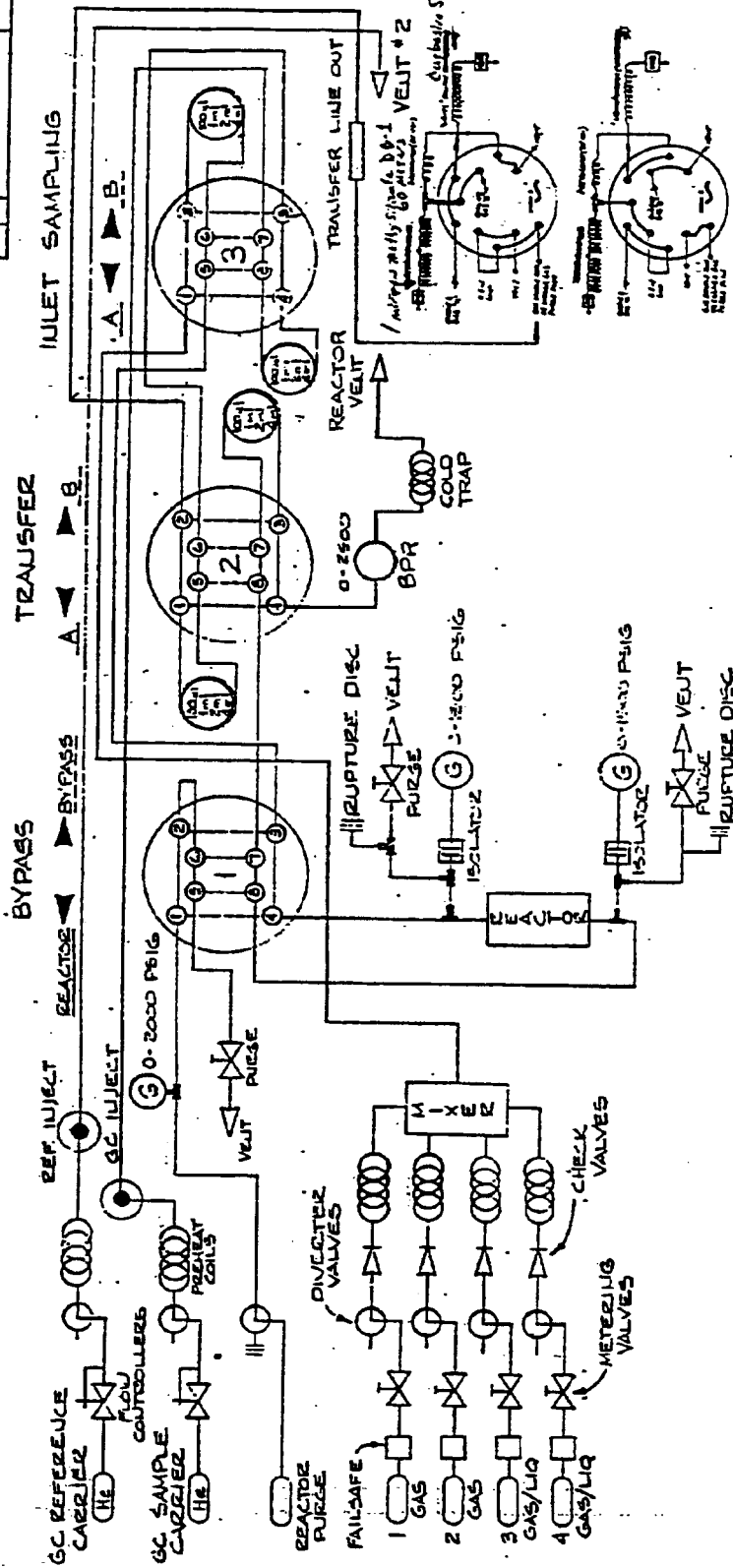


*8 channel 16 Bit resolution
 A-D converter P6L
 4 channel D-A (12 bit)

Tape record of system conditions for emergency (off line) evaluation

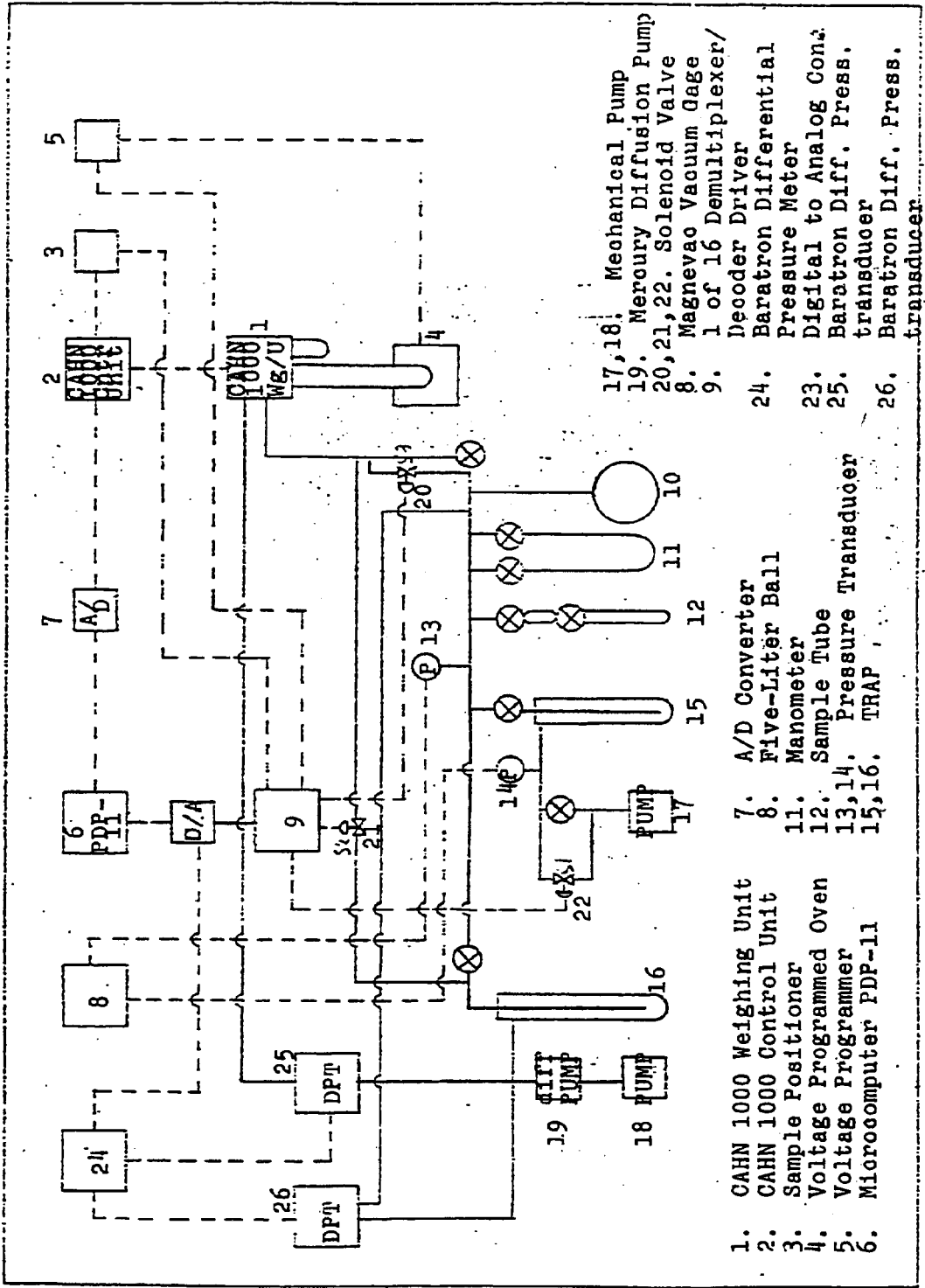
CD6 804CF CONTINUOUS FLOW REACTION SYSTEM

DATE	REVISED	REVISION RECORD	AUTHOR	DATE



TOLERANCES UNLESS SPECIFIED	CHEMICAL DATA SYSTEMS, INC. OXFORD, PA. 19303	
DECIMAL	SCALE	DRAWN BY
FRACTIONAL		APPROVED BY
ANGULAR	TITLE	
	DATE	DRAWING NUMBER
	6-4-82	CD6 803CF
		B-0803-801009-0

Figure 3



- 17, 18. Mechanical Pump
- 19. Mercury Diffusion Pump
- 20, 21, 22. Solenoid Valve
- 8. Magnevac Vacuum Gage
- 9. 1 of 16 Demultiplexer/Decoder Driver
- 24. Baratron Differential Pressure Meter
- 23. Digital to Analog Converter
- 25. Baratron Diff. Press. transducer
- 26. Baratron Diff. Press. transducer

- 1. CAHN 1000 Weighing Unit
- 2. CAHN 1000 Control Unit
- 3. Sample Positioner
- 4. Voltage Programmed Oven
- 5. Voltage Programmer
- 6. Microcomputer PDP-11
- 7. A/D Converter
- 8. Five-Liter Ball
- 11. Manometer
- 12. Sample Tube
- 13, 14. Pressure Transducer
- 15, 16. TRAP

Figure 4

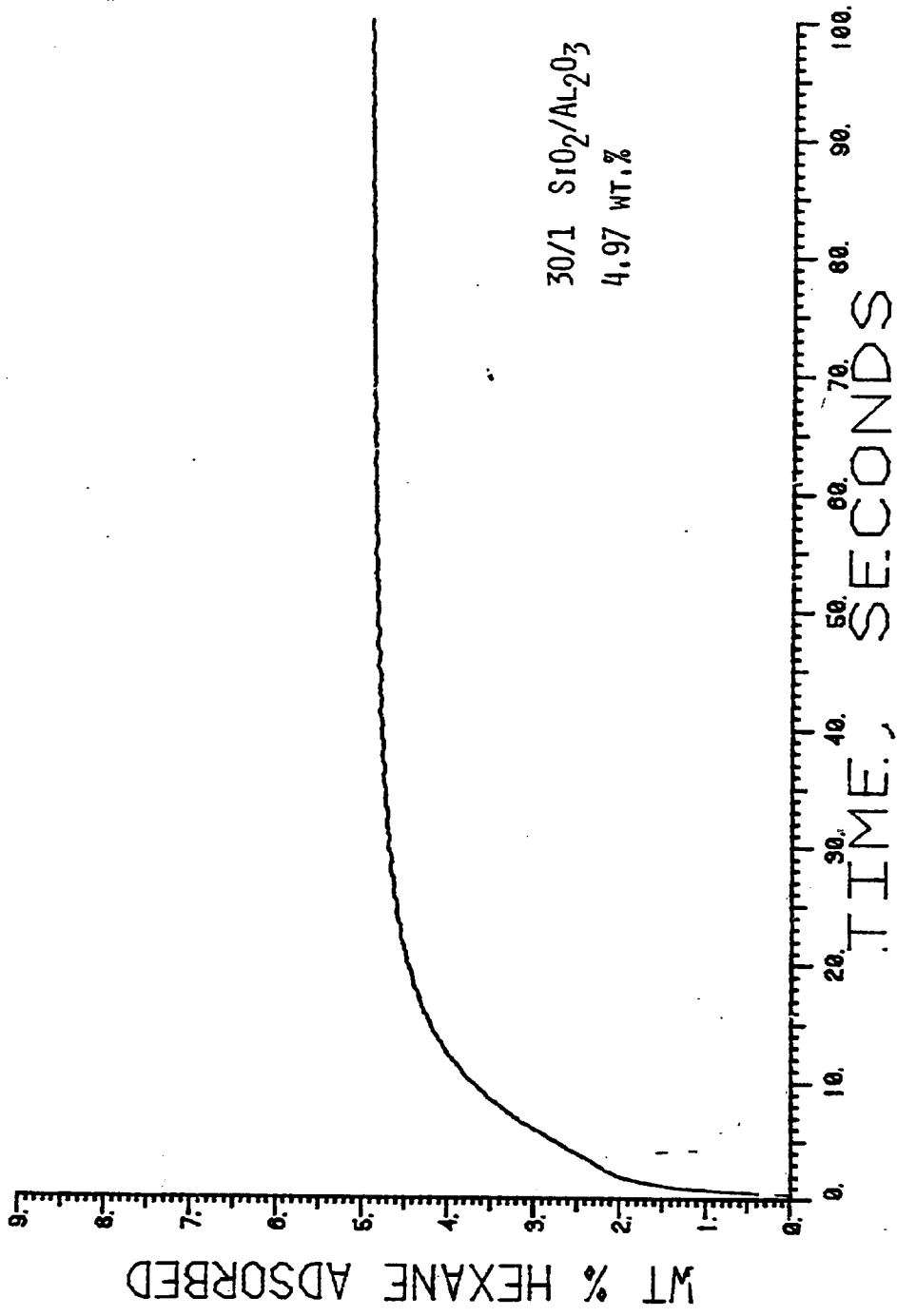


Figure 5

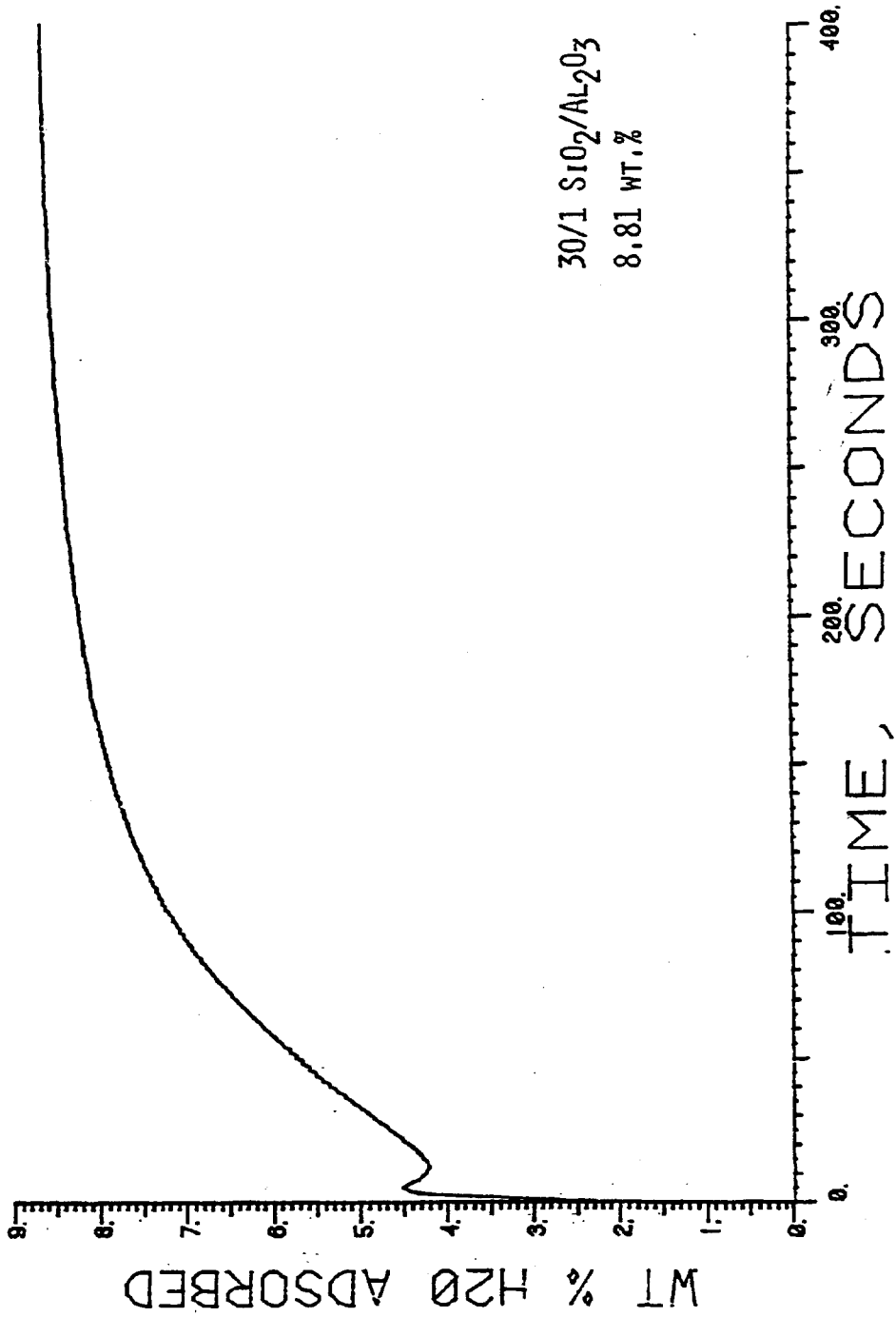


Figure 6

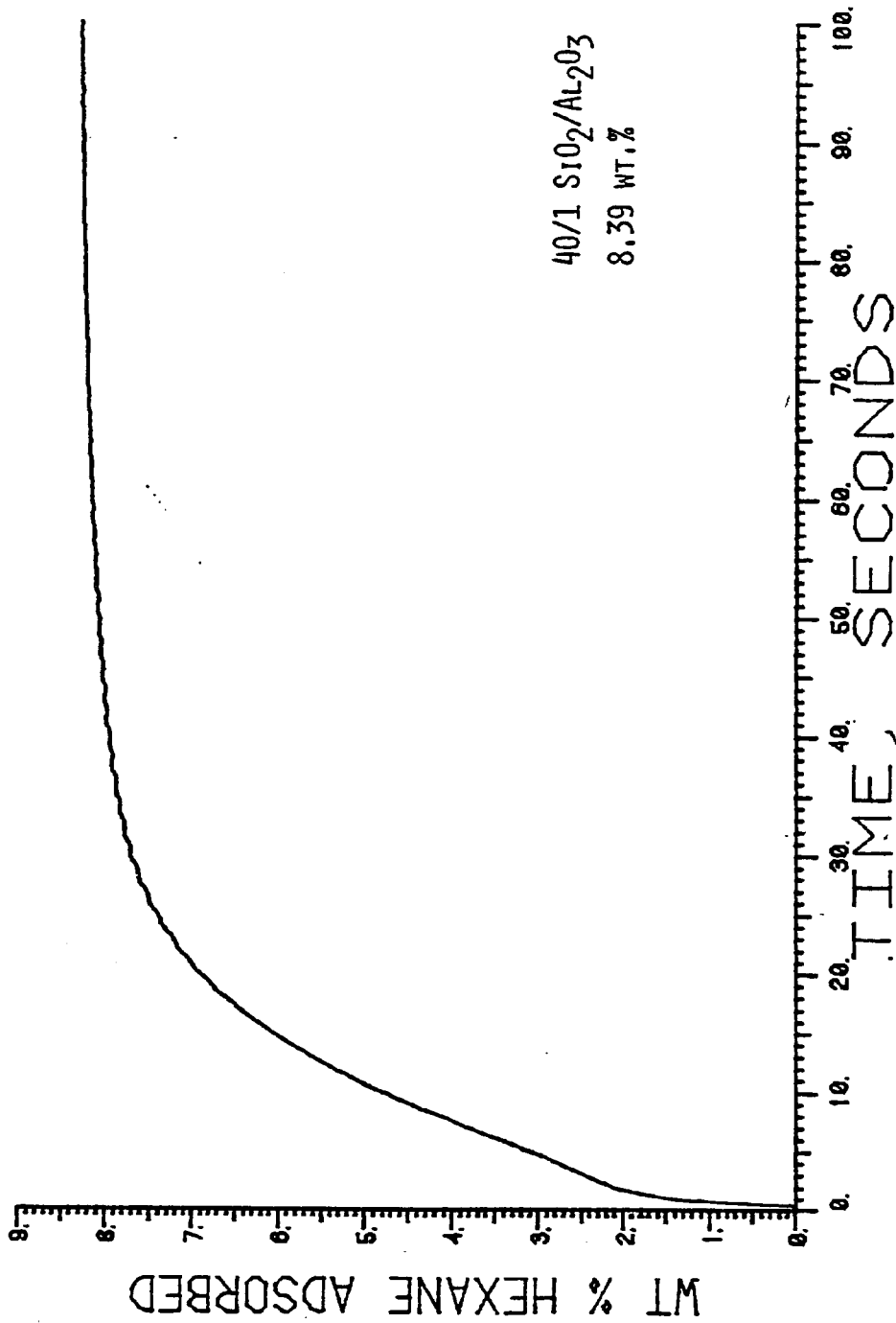


Figure 7

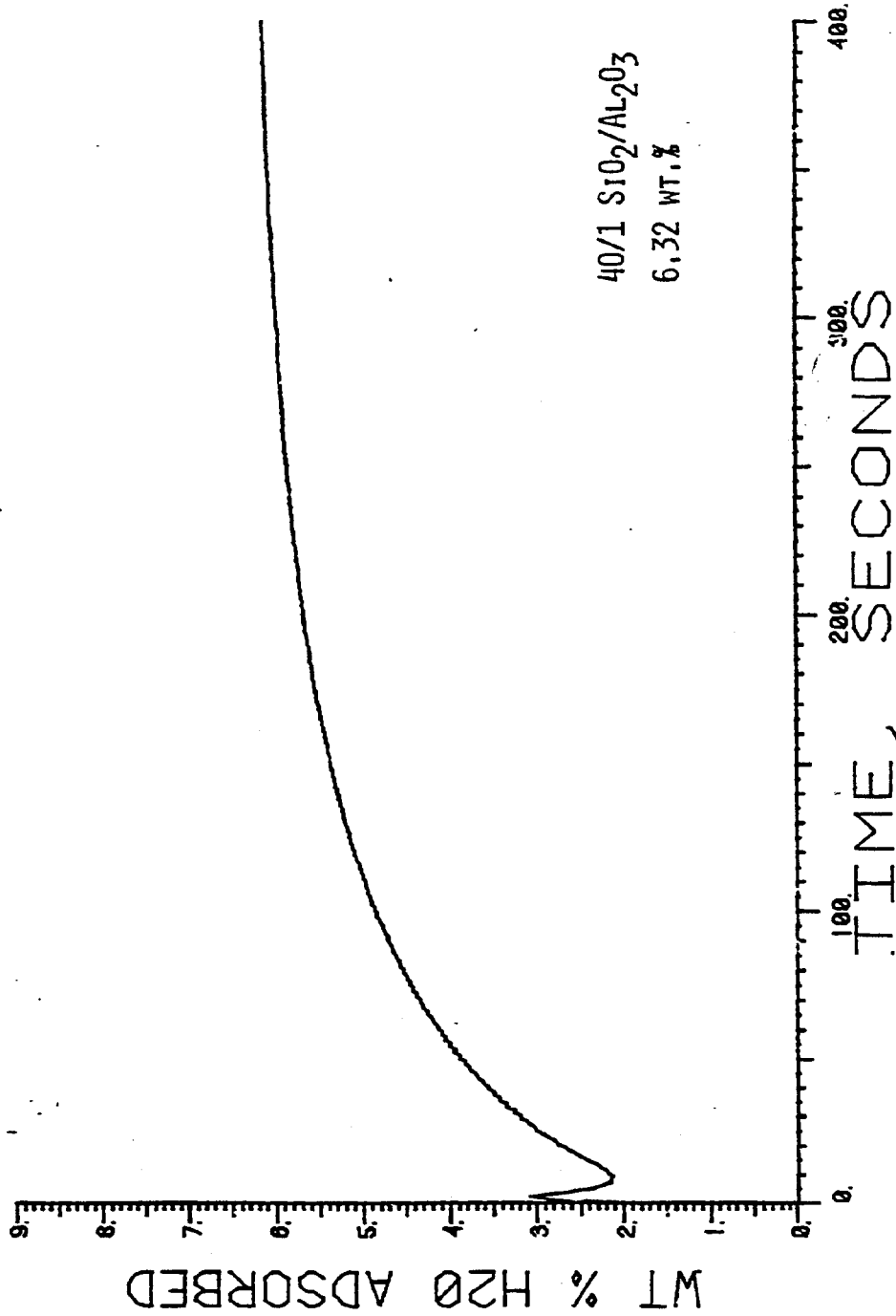


Figure 8

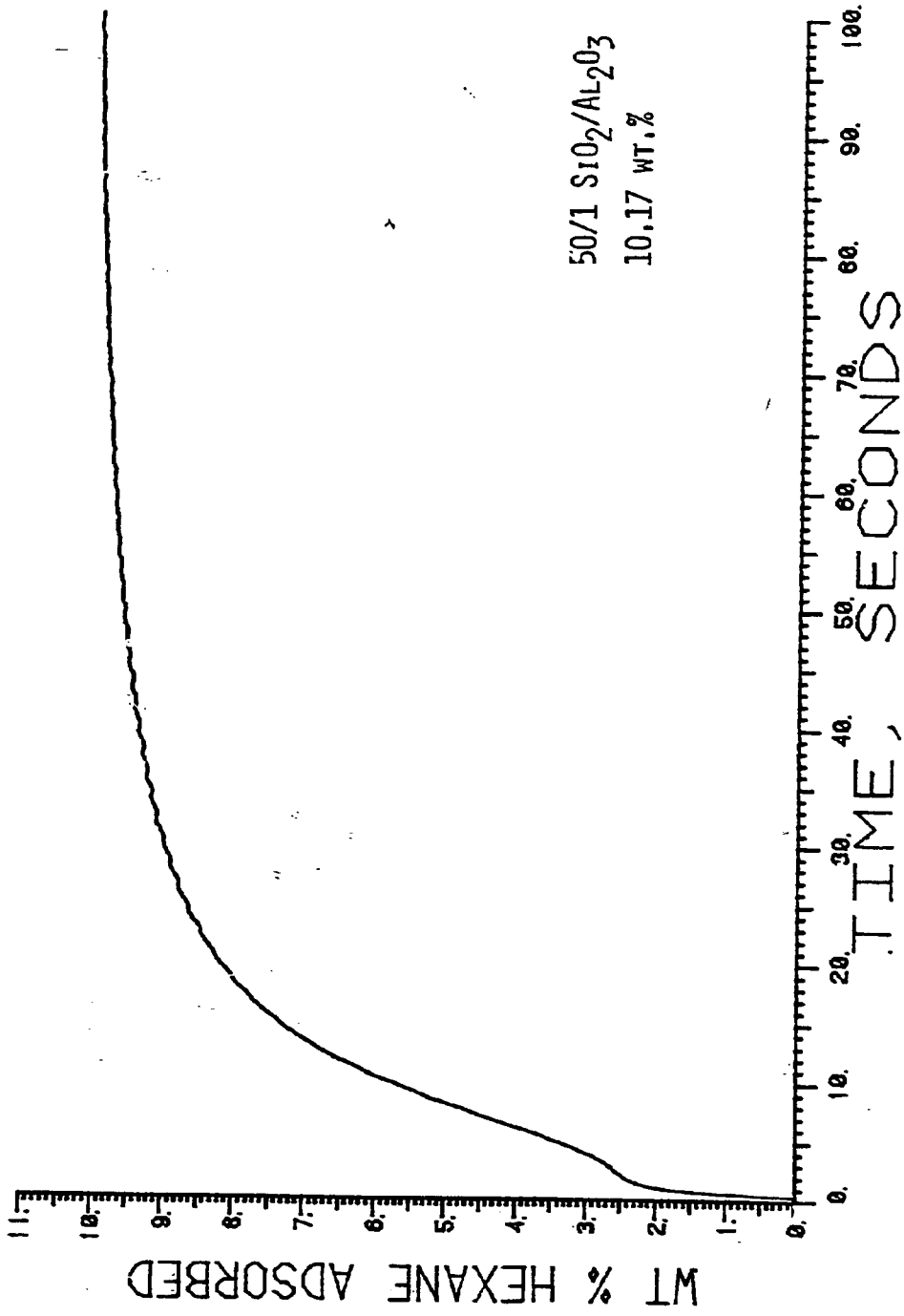


Figure 9

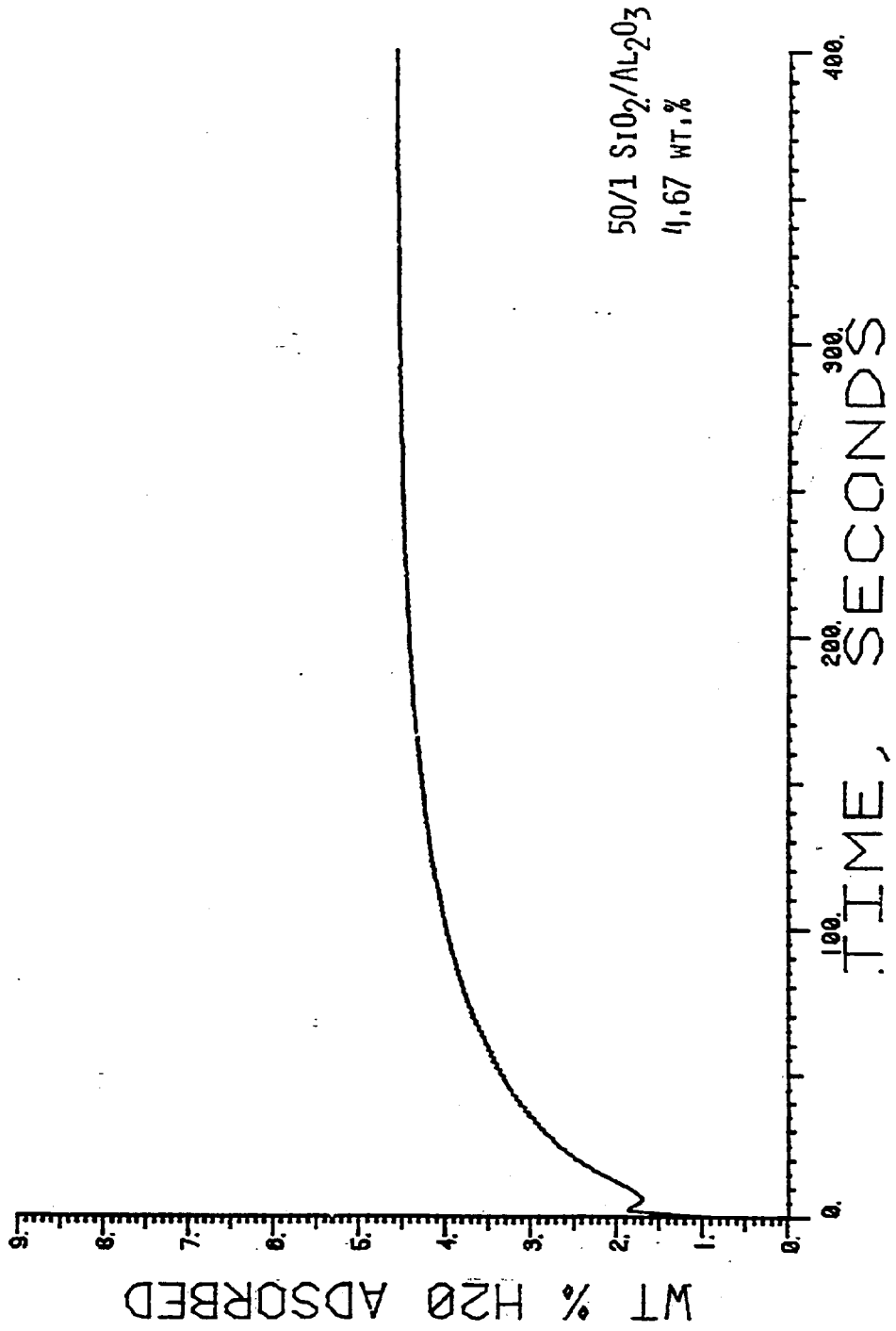


Figure 10

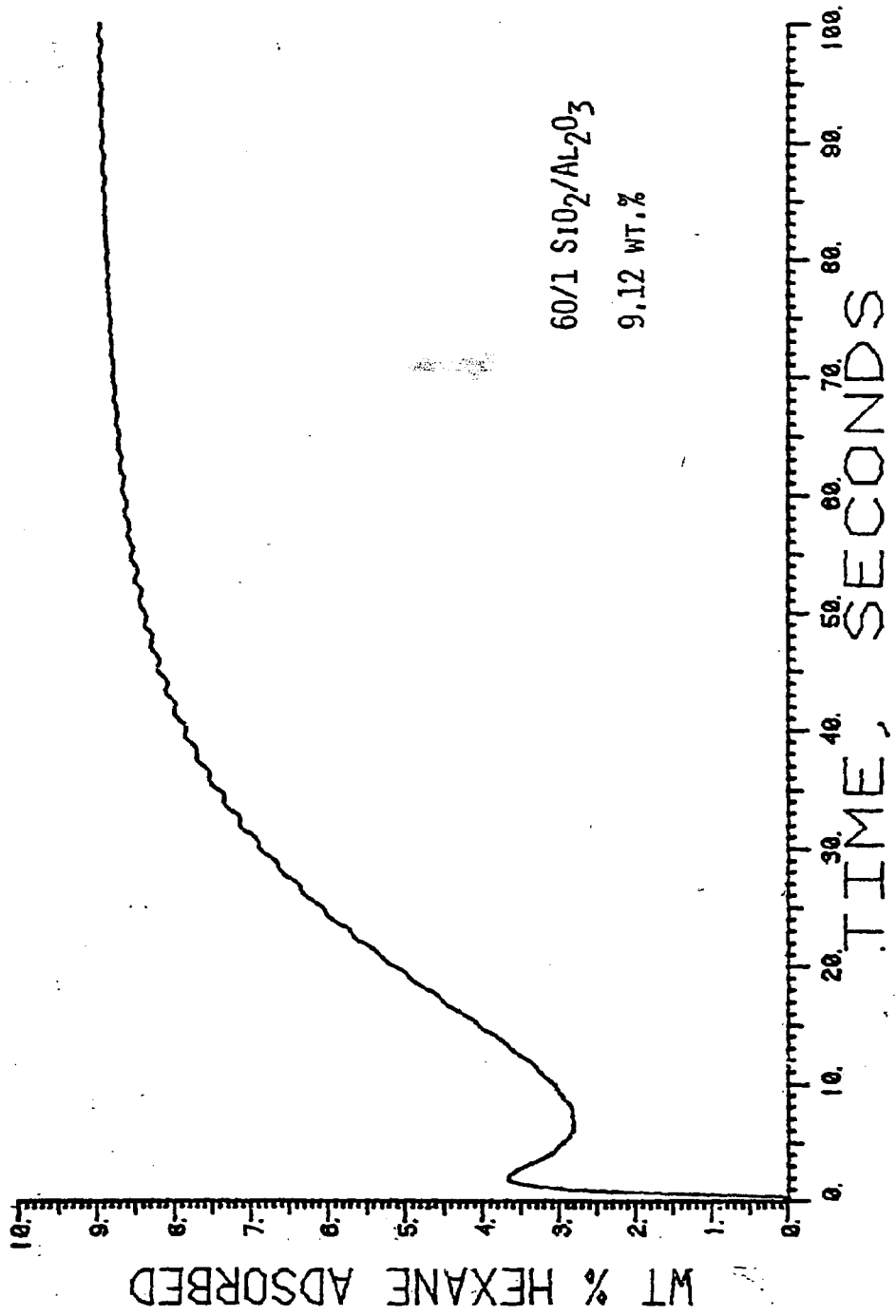


Table 1

NEAR - EQUILIBRIUM ADSORPTION CAPACITIES (g/100g)

FOR ZSM-5 SYNTHESIZED WITH VARYING $\text{SiO}_2/\text{Al}_2\text{O}_3$ RATIOS.

24 MIN., 6.5 TORR.

<u>$\text{SiO}_2/\text{Al}_2\text{O}_3$</u>	<u>H_2O</u>	<u>N-HEXANE</u>	<u>% CRYSTALLINITY BY XRD</u>
30/1	8.8	5.0	51
40/1	6.3	8.4	63
50/1	4.7	10.2	70
60/1	3.4	9.1	82

Table 2

TWO THETA	INTENSITY	D-SPACING
21.06	5.660	4.2148
21.26	7.311	4.1756
21.71	1.061	4.0900
22.06	2.240	4.0259
22.41	5.307	3.9638
22.56	5.660	3.9378
22.81	12.972	3.8952
23.11	51.297	3.8453
23.41	100.000	3.7967
23.56	47.170	3.7729
23.91	18.986	3.7184
24.06	26.062	3.6956
24.16	35.259	3.6805
24.46	8.608	3.6361
24.66	51.416	3.6070
25.06	1.769	3.5503
25.76	4.363	3.4554
26.11	13.208	3.4099
26.26	14.622	3.3908
26.56	3.184	3.3531
26.91	5.424	3.3103
27.11	6.368	3.2863

848.

Figure 13

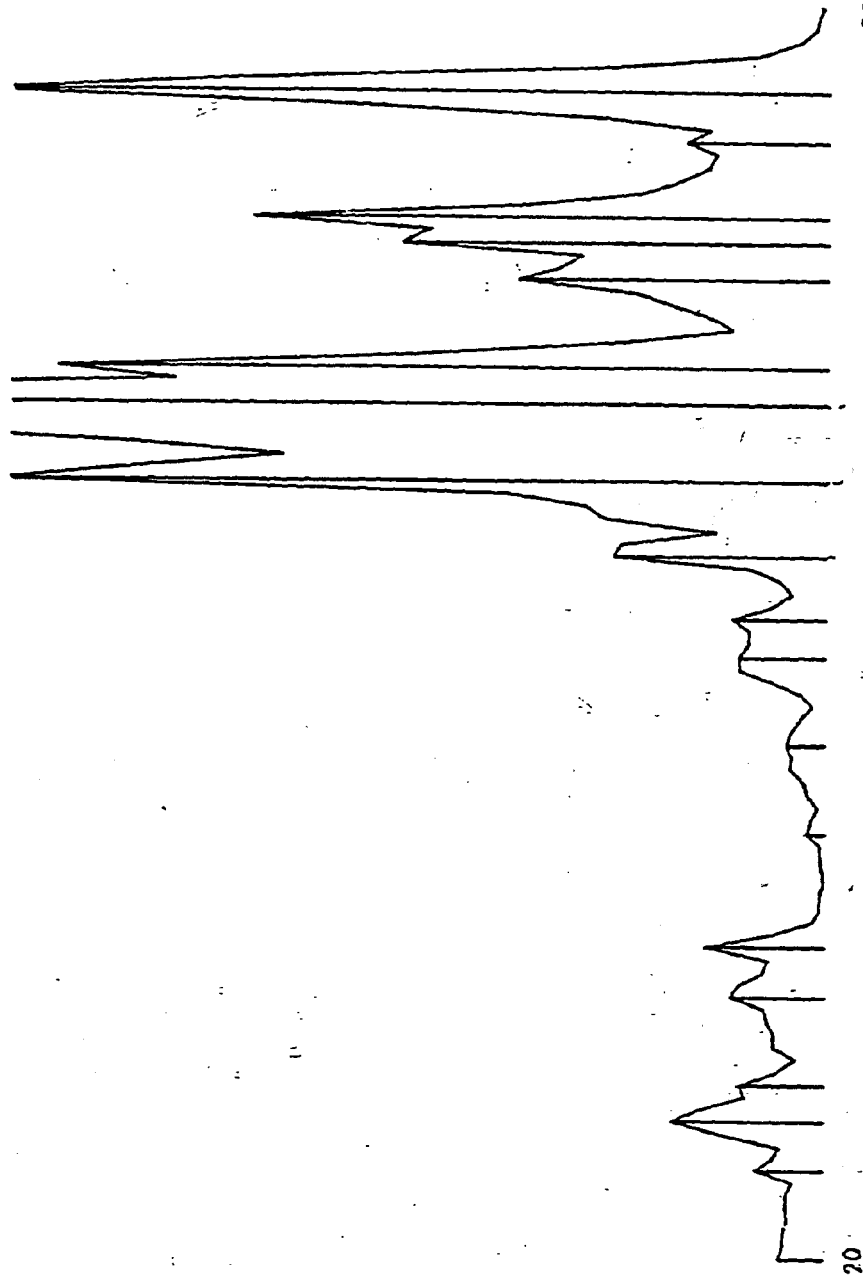


Figure 11

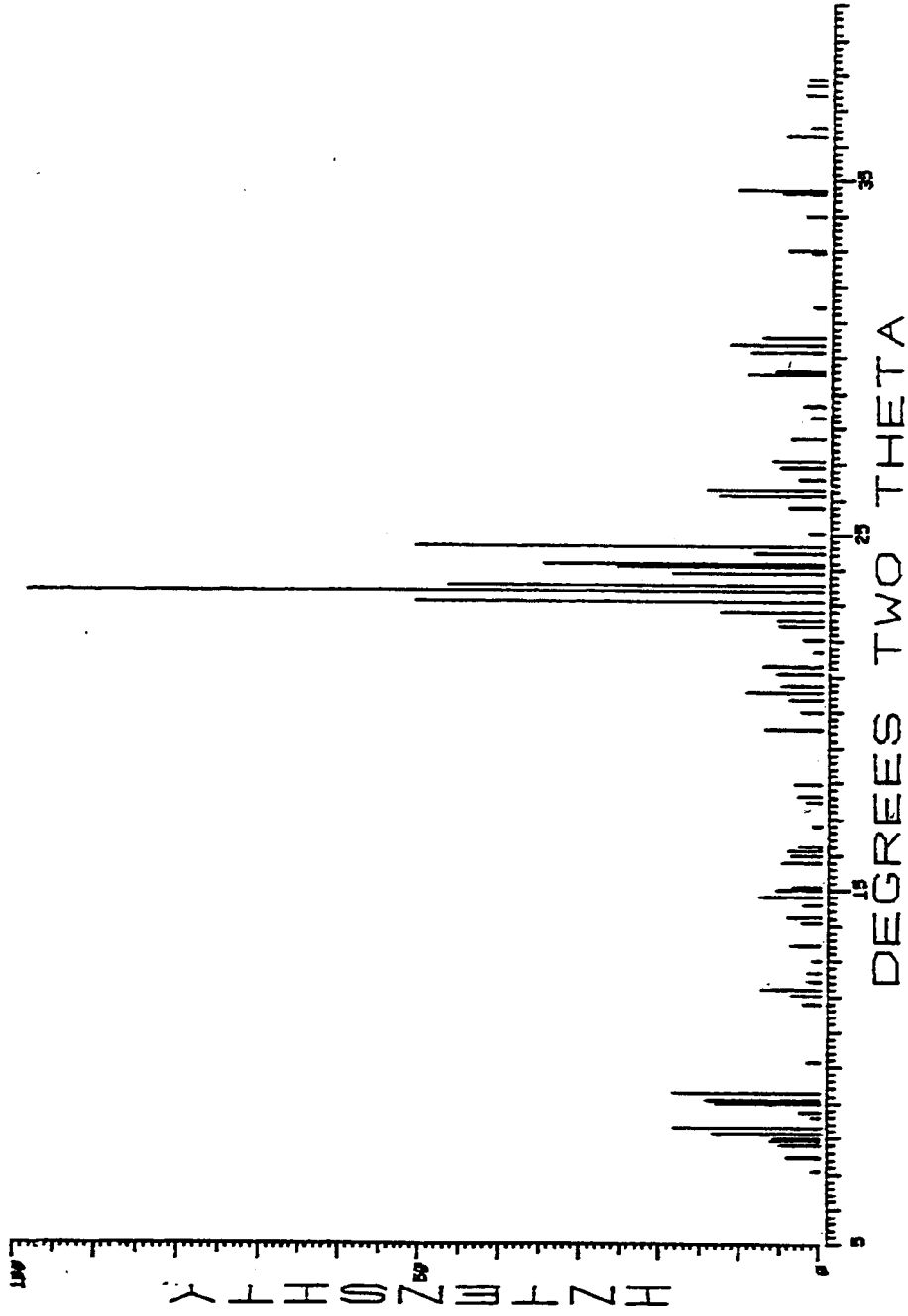


Figure 12

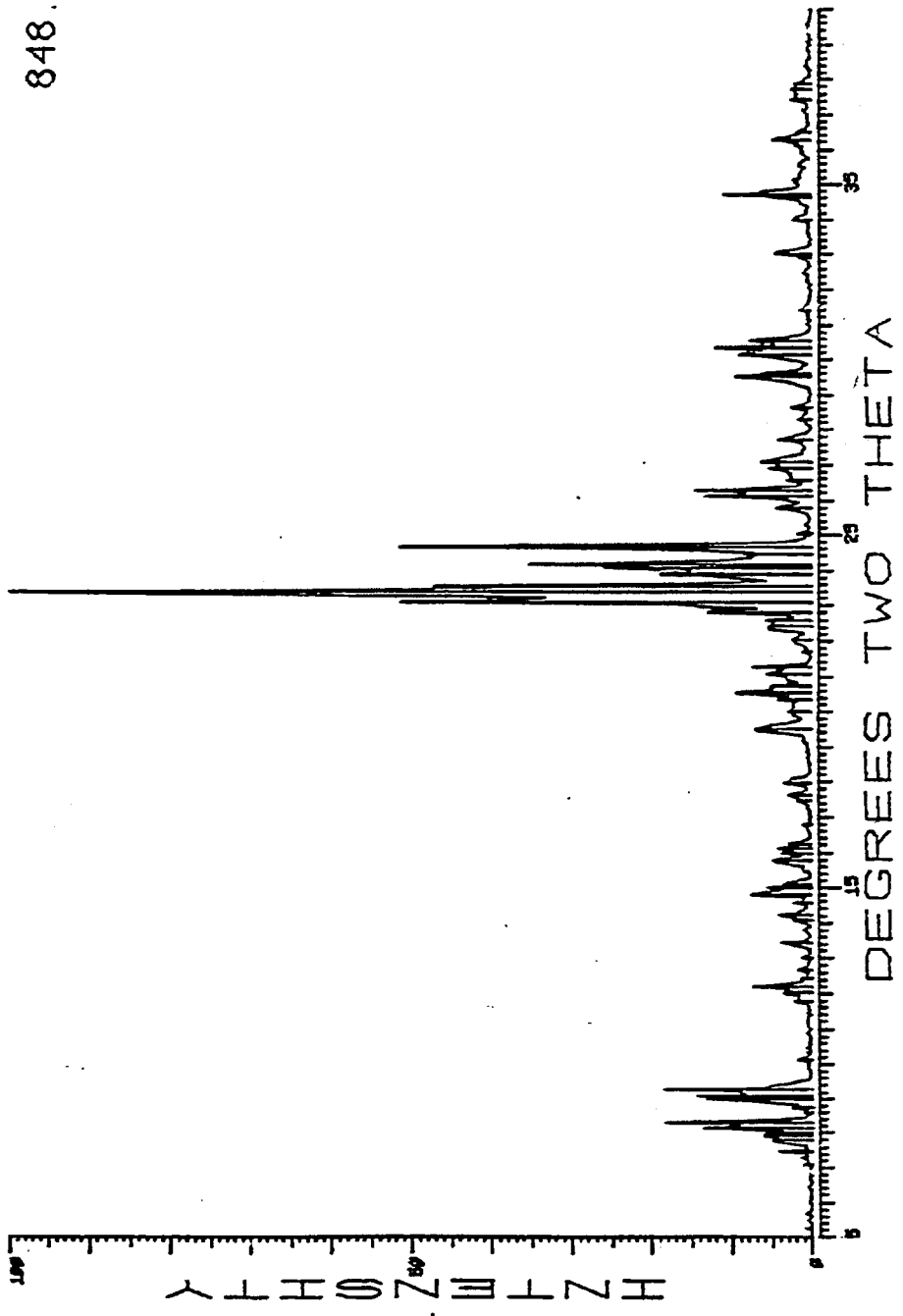


Plate 3

SEM 21)

Shows cobalt thoria impregnated silicalite single crystal. Impregnation solution composition 15.26 gms Co $(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, 1.03 gms Th $(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$ per 500 ml acetone at 120 C. Crystal has fractured surface exposed.

SEM 22)

Higher magnification of crystal in SEM 21. Spots a - g and field h given in analyses 11 through 18.

SEM 23)

Cobalt thoria impregnated silicalite. Impregnation temperature 120 C and solution composition 15.26 gms Co $(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, 1.03 gms Th $(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$ per 500 ml acetone..

SEM 24)

Close-up of SEM 23 showing fractured crystal surface. Analysis of spots a-g (excluding e) appear in analyses 19 through 24.

SEM 25)

Shows same silicalite crystal as in SEM 24. at a different orientation.

SEM 26)

Shows back scatter image of same crystal as in SEM 24 and 25. Analysis of spots a-h appear in analyses 25-32. Comparing this fractured surface to SEM given in 24, one can see there is at least 20 microns of depth below these analyses spots. Since the maximum tear drop depth below the analysis beam is 6 microns, we can be assured we're not observing the metals on the far side of the crystal.



Plate 4

Analysis 25)
Analysis of spot A in SEM 26 shows higher level of thorium than cobalt on fractured surface.

Si
Au Th Co

Analysis 27)
Analysis of spot C on crystal in SEM 26 shows higher level of thorium than that of cobalt inside crystal.

Th Co

Analysis 29)
Analysis of spot E on crystal in SEM 26 indicates thorium has moved all the way to the center of the crystal.

Si
Au Th Co

Analysis 31)
Analysis of spot G on fractured surface of crystal in SEM 26 shows thorium is present and cobalt is absent.

TH Co

Analysis 26)
Analysis of spot B of fractured surface of crystal in SEM 26 shows higher level of thorium than cobalt.

Si
Au Th Co

Analysis 28)
Analysis of spot D on crust covering outer surface of crystal in SEM 26 shows it to contain a high level of cobalt.

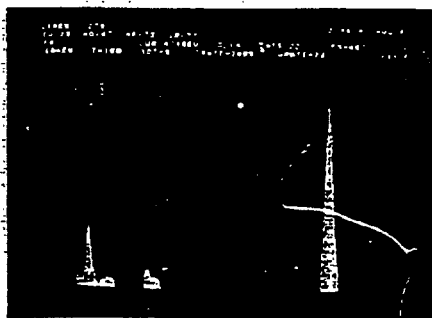
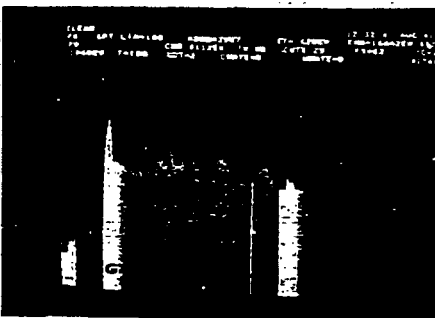
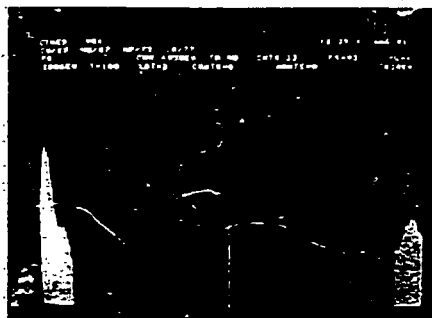
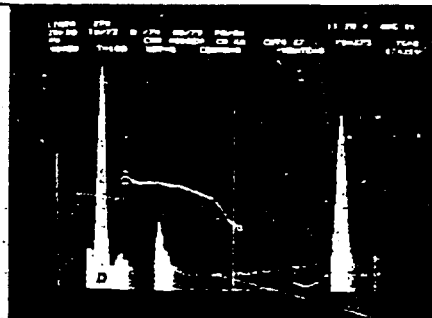
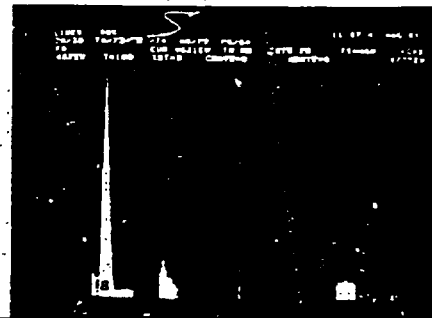
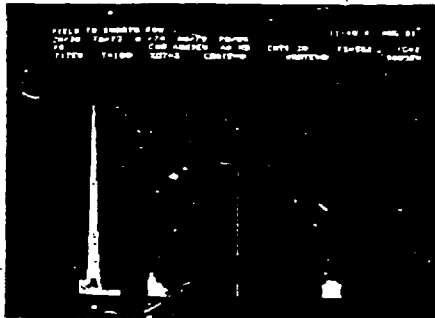
Si
Au Th Co

Analysis 30)
Analysis of spot F inside crystal shown in SEM 26 shows a higher relative level of thorium to that of cobalt.

TH Co

Analysis 32)
Analysis of spot H of crust covering crystal in SEM 26 shows it to be predominately cobalt.

Si
Au Th Co



ZSM-5 SYNTHESIS SYSTEMS

1972	ARGAUER & LANDOLT	TPA - NA
1977	GROSE & FLANIGEN	TPA - NA (K, NH ₄)
1979	ROLLMANN & VOLYCOSIK	(1,6 HEXANEDIAMINE) - NA
	PLANK, ROSINSKI, RUBIN	ETHANOL - NA
	ERDEM & SAND	TPA - K ₂ O
	RUBIN, ROSINSKI, PLANK	(N-(C ₂ -C ₉)AMINE) - NA
1980	BIBBY, MILESTONE, ALDRIDGE	TPA - NH ₄
1981	GROSE & FLANIGEN	NA (LI, BA)
1982	DESSAU	N-PROPYL BR
		TRI-N-PROPYLAMINE
		METHYL ETHYL KETONE
		} NA
	NASTRO & SAND	TPA - NH ₄ = LI
	MOSTOWICZ & SAND	TPA - BaO, TPA - SrO

PARAMETERS PROMOTING GROWTH

- NON-AGITATED RX
- VISCOUS REACTANT SYSTEM
- Na, K, NH₄ ADDITIONS
(TO SOME SYSTEMS)
- Cl, CO₃, HCO₃ ADDITIONS
(TO SOME SYSTEMS)

ZEOLITE PARTICULATION

APPROACH

- . BY DIRECT SYNTHESIS
 - . SINGLE CRYSTALS
 - . CRYSTAL AGGREGATES
 - . PSEUDOMORPHIC CONVERSION
- . HIGH YIELD
- . UNIFORM SIZE
- . PROPERTIES
 - SPORTION
 - CATALYTIC
- . CORRELATION

PARAMETERS

PRESSURE

AUTOGENOUS ONLY

TEMPERATURE

75 - 200 °C

COMPOSITION

NA	TRH-OH	AL ₂ O ₃	SiO ₂	H ₂ O	CL
K					BR
NH ₄					CO ₃

REACTANTS:	ALUMINATE	INDEX
	REHEISGEL	QUSO

TIME

1 - 500 HRS

PARAMETERS PROMOTING GROWTH

- NON-AGITATED RX
- VISCOUS REACTANT SYSTEM
- Na, K, NH₄ ADDITIONS
(TO SOME SYSTEMS)
- Cl, CO₃, HCO₃ ADDITIONS
(TO SOME SYSTEMS)

Table 5

12 Na₂O - 4.5(TPA)₂O·Al₂O₃ - 90 SiO₂

LUDOX, TPABR⁻ 500-2000 H₂O

QUSO, TPAOH 1000-4500 H₂O

SPHERULITES ~1 μM

6 Na₂O - 6(NaHCO₃)₂ [] 400 H₂O

SUBHEDRAL 80 μM

CH₃CO₂ SPHERULITES 4-5 μM

SO₄ " 8-10

CO₃ DISCS 14

CL " 10-15

CO₃, CL SPHERULITES 2-10

Table 6

4(TPA)₂O - 40 SiO₂ - 750 H₂O

DISC INTERGROWTHS 3-4 μM

10(TPA)₂O - Al₂O₃ - 59 SiO₂ - 750 H₂O

SPHERULITES < 1 μM

5(TPA)₂O - 5 (NH₄)₂O - 90 SiO₂ - 750 H₂O

DISC INTERGROWTH 3-4 μM

4(TPA)₂O - 60 (NH₄)₂O - 90 SiO₂ - 750 H₂O

EUHEDRAL LATHS 30-40 μM

8(TPA)₂O - 38-60 (NH₄)₂O - (0-1.5) (NA OR K)₂O -
59 SiO₂ - 750 H₂O

No ADDITION 3-4 μM

1 Na₂O }
1 K₂O } 30-40 μM

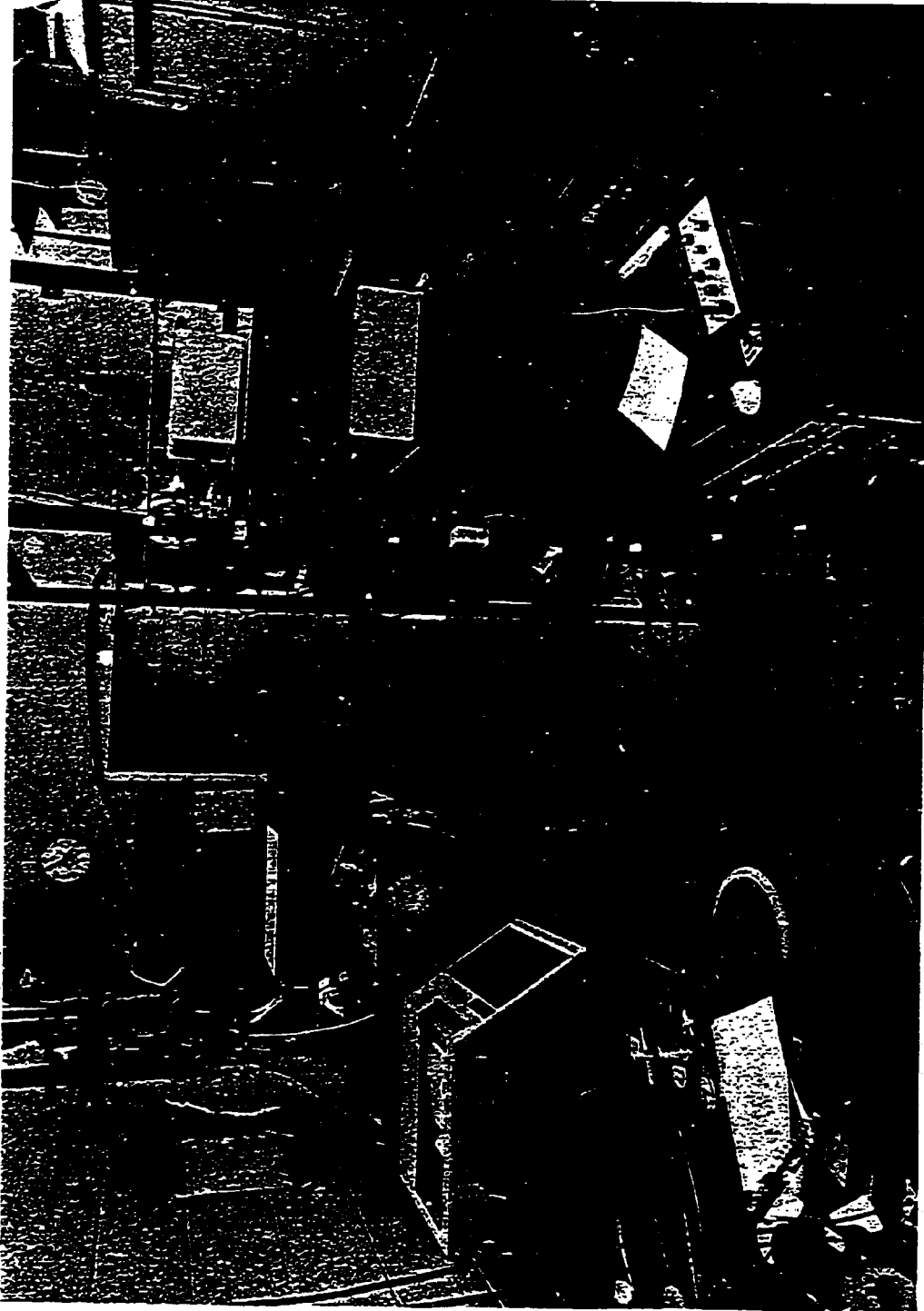
Table 7

$6.5(\text{Na}_2\text{O}) - \text{Al}_2\text{O}_3 - (60-100) \text{SiO}_2 (200-500) \text{H}_2\text{O}$

EUHEDRAL, DISC INTERGROWTHS 20-40 μM

$3.25 \text{Na}_2\text{O} - 3.25 (\text{TPA})_2\text{O} - [\quad]$

TO 25 μM SPHERULITIC INTERGROWTHS





CONCLUSIONS

- EXPLORATORY SYNTHESIS PRODUCED ZSM-5
 - IN MANY SYSTEMS
 - WIDE RANGE OF Si/Al
 - WIDE PARTICLE SIZE RANGE
- OPERABLE
 - COMPUTERIZED XRD
 - COMPUTERIZED CAHN ADSORPTION BALANCE
 - NEAR COMPLETION - DEC COMPUTERIZED MICROPLANT REACTOR SYSTEM

FUTURE PROGRAM

- INCORPORATE TRANSITION METALS
- LARGE BATCH SYNTHESIS
- CATALYTIC ACTIVITY
- OPTIMIZATION OF MATERIAL AND PROCESS PARAMETERS