

APPENDIX D

HYDROTHERMAL SYSTEMS INVESTIGATED FOR THE SYNTHESIS
OF ZSM-5

Table 26 Summary of Par Autoclave Runs for Synthesis of Varying Silica to Alumina Ratio

Run #	Page in Lab Book	Molar Composition	Composition in Gms Reagent	SiO ₂ /Al ₂ O ₃	X-Ray Analysis Fig. #
P1	15	3.10 Na ₂ O 1.00 Al ₂ O ₃ 27.91 SiO ₂ 1163.08 H ₂ O	410.92 Ludox AS 16.65 Sodium Aluminate 504.59 TPA Br 12.84 NaOH 1182.23 H ₂ O	27.9:1	1
P2	33	3.10 Na ₂ O 1.00 Al ₂ O ₃ 27.91 SiO ₂ 1163.08 H ₂ O 12.406 TPABr	451.85 Ludox LS 18.31 Sodium Aluminate 277.43 TPABr 14.12 NaOH 1300.00 H ₂ O	27.9:1	2
P3	50	3.5 Na ₂ O 1.5 Al ₂ O ₃ 30.0 SiO ₂ 1200.0 H ₂ O 29.2 TPABr	367.91 Ludox LS 20.80 Sodium Aluminate 494.71 TPABr 10.18 NaOH 1000.00 H ₂ O	20:1	3
P9	70	3.59 Na ₂ O 1.00 Al ₂ O ₃ 20.00 SiO ₂ 1872.11 H ₂ O	156.35 Ludox LS 8.51 Sodium Aluminate 167.66 TPABr 8.09 NaOH	20:1	4

Table 26
Continued

Run #	Page in Lab Book	Molar Composition	Composition in Gms Reagent	SiO ₂ /Al ₂ O ₃	X-ray Analysis Fig. #
P10	70	17.00 TPA Br 3.59 Na ₂ O 1.00 Al ₂ O ₃ 30.00 SiO ₂ 1872.11 H ₂ O 17.00 TPABr	1203.37 H ₂ O 245.70 Ludox Ls 8.91 Sodium Aluminate 185.08 TPABr 8.48 NaOH 1203.37 H ₂ O	30:1	5 Fig 6 shows- P10 after Ammonium Chloride ex- change
P11	70	3.59 Na ₂ O 1.00 Al ₂ O ₃ 40.00 SiO ₂ 187.11 H ₂ O 17.00 TPABr	344.00 Ludox Ls 9.36 Sodium Aluminate 194.34 TPABr 8.90 NaOH 1203.37 H ₂ O	40:1	7 358
P12	70	3.59 Na ₂ O 1.00 Al ₂ O ₃ 50.00 SiO ₂ 1872.11 H ₂ O 17.00 TPABr	462.64 Ludox Ls 9.85 Sodium Aluminate 204.58 TPABr 9.37 NaOH 1203.37 H ₂ O	50:1	8
P13	71	3.59 Na ₂ O 1.00 Al ₂ O ₃ 60.00 SiO ₂ 1872.11 H ₂ O 17.00 TPABr	573.38 Ludox Ls 9.85 Sodium Aluminate 215.95 TPABr 9.89 NaOH 1203.37 H ₂ O	60:1	9 Fig 10 show: P13 after Ammonium Chloride ex- change

Table 26
Continued

X-ray Analysis

Run #	Page in Lab Book	Molar Composition	Composition in Gms Reagent	SiO ₂ /Al ₂ O ₃	Fig. #
P14	71	3.59 Na ₂ O 1.00 Al ₂ O ₃ 70.00 SiO ₂ 1872.11 H ₂ O 17.00 TPABr	588.61 Ludox Ls 9.15 Sodium Aluminate 190.02 TPABr 8.71 NaOH 1000.00 H ₂ O	70:1	
P15	71	3.59 Na ₂ O 1.00 Al ₂ O ₃ 80.00 SiO ₂ 1872.11 H ₂ O 17.00 TPABr	860.15 Ludox Ls 11.70 Sodium Aluminate 242.97 TPABr 11.13 NaOH 1203.37 H ₂ O	80:1	
P16	71	3.59 Na ₂ O 1.00 Al ₂ O ₃ 90.00 SiO ₂ 1872.11 H ₂ O 17.00 TPABr	856.80 Ludox Ls 10.37 Sodium Aluminate 215.38 TPABr 9.87 NaOH 1000.00 H ₂ O	90:1	
P17	72	3.59 Na ₂ O 1.00 Al ₂ O ₃ 100.00 SiO ₂ 1872.11 H ₂ O 17.00 TPABr	919.14 Ludox Ls 10.00 Sodium Aluminate 207.71 TPABr 9.52 NaOH 900.00 H ₂ O	100:1	

Table 26
Continued

Run #	Page in Lab Book	Molar Composition	Composition in Gms Reagent	X-ray Analysis	
				SiO ₂ /Al ₂ O ₃	Fig. #
P18	72	3.59 Na ₂ O 1.00 Al ₂ O ₃ 150.00 SiO ₂ 1872.11 H ₂ O 17.00 TPABr	1669.07 Ludox Ls 12.11 Sodium Aluminate 251.45 TPABr 11.52 NaOH 700.00 H ₂ O	150:1	
P21	106	3.5 Na ₂ O 1.5 Al ₂ O ₃ 30.00 SiO ₂ 1200.00 H ₂ O 29.20 TPABr	417.82 Ludox Ls 22.74 Sodium Aluminate 540.16 TPABr 11.13 NaOH 1203.00 H ₂ O	20:1	11 360
P22	107	5.00 Na ₂ O 3.00 Al ₂ O ₃ 30.00 SiO ₂ 1200.00 H ₂ O 41.70 TPABr	419.79 Ludox Ls 45.69 Sodium Aluminate 775.75 TPABr 11.18 NaOH 1203.00 H ₂ O	10:1	12

Table 27
Lab Book

Exploratory Runs

Run #	Pg.#	Na ₂ O	Al ₂ O ₃	SiO ₂	H ₂ O	TPA ₂ O	SiO ₂ / Al ₂ O ₃	Fig. #
DOD6	35	2.00	0.65	18.00	750.00	8.00	27.7:1	17
DOD8	25	2.00	0.16	18.00	750.00	4.00	111:1	13
DOD7	24	2.00	0.18	18.00	750.00	4.00	100:1	
DOD9	28	2.00	0.162	18.00	750.00	4.00	111:1	
DOD10	28	2.00	0.13	18.00	750.00	4.00	143:1	
DOD12	29	2.00	0.03	18.00	750.00	4.00	666.7:1	14
DOD13	30	2.00	0.23	18.00	750.00	4.00	80:1	15
DOD14	31	2.00	0.30	18.00	750.00	4.00	60:1	
DOD15	31	2.00	0.45	18.00	750.00	4.00	40:1	16
DOD16	36	1.00	0.00	18.00	350.00	2.00	infinity	18
DOD18	48	10.00	0.00	100.00	4170.00	20.00	infinity	19
DOD19	48	12.2	0.00	100.00	4170.00	24.5	infinity	20
DOD20	49	13.3	0.00	100.00	4170.00	26.6	infinity	21
DOD21	49	14.4	0.00	100.00	4170.00	28.8	infinity	22
DOD24	56	11.00 SiO ₂ : Al (Na(O ₃)) ₃ : 2 NaOH : 72 (TPA)OH : 5074.84 H ₂ O						
DOD25	57	11.00 SiO ₂ : Al (Na(O ₃)) ₃ : 2 NaOH : 72 (TPA)OH : 3300.00 H ₂ O						23
DOD26	60	2.00	0.00	18.00	1500.00	4.00	infinity	24
DOD27	61	4.00	0.00	18.00	1500.00	8.00	infinity	
DOD28	61	3.00	0.00	18.00	1500.00	8.00	infinity	

Table 27
Exploratory Runs
Continued
Lab Book

Run #	Pg. #	Na ₂ O	Al ₂ O ₃	SiO ₂	H ₂ O	TPA ₂ O	SiO ₂ / Al ₂ O ₃	Fig. #
DOD29	62	3.00	0.00	18.00	1500.00	6.00	infinity	
DOD30	81	2.00	0.00	18.00	700.00	8.00	infinity	
DOD31	82	11.11	1 as ni- trate	100.00	3888.00	44.5	100:1	
DOD32	82	11.11	.5 as ni- trate	100.00	3888.00	44.5	200:1	25
DOD33	83	11.11	5 as ni- trate	100.00	3888.00	44.5	20:1	26
DOD34	83	11.11	3.3 as ni- trate	100.00	3888.00	44.5	30:1	27
DOD35	83	11.11	2.00	100.00	3888.00	44.5	50:1	28
DOD36	83	11.11	1.11	100.00	3888.00	44.5	90:1	29
DOD37	87	(See note- book through DOD42)						30
DOD38	87							31
DOD39	87							32
DOD40	87							33
DOD41	87							34
DOD42	87							35
DOD43	104	Aluminum added as Al(NO ₃) ₃ · 9 H ₂ O aluminum nitrate						36
DOD44	104	Aluminum added as aluminum iso-propoxide Al/OCH(CH ₃) ₂ /3						37
DOD45	104	Aluminum added as aluminum ammonium sulfate						38
		Al ₂ (SO ₄) ₃ · (NH ₄) ₂ SO ₄ · 24H ₂ O						
DOD46	104	Aluminum added as aluminum hydroxide Al ₂ O ₃ · 3 H ₂ O						39
DOD47	104	Aluminum added as aluminum chloride AlCl ₃ · 6 H ₂ O						40

Table 27
Exploratory Runs
Continued
Lab Book

Run #	Pg.#	Na ₂ O	Al ₂ O ₃	SiO ₂	H ₂ O	TPA ₂ O	SiO ₂ / Al ₂ O ₃	Fig.#
DOD48	104	Aluminum added as aluminum metal						41
DOD49	104	2.00	0.00	18.00	750.00	8.00	infinity	
DOD51	108	5.75	3.75	30.00	1200.00	47.96	8:1	42
DOD52	108	8.00	6.00	30.00	1200.00	66.72	5:1	43

Table 28. Batch Compositions

DOD-N1-ZSM-5-1

TPABr	107
NH ₄ OHBr	600 cc
F-2000	4.75
LudoxAS-40	442
NaOH	10.8
Ni ²⁺ SO ₄ · 6H ₂ O 60 gr (7.5 wt.% Ni) (263MW)	

DOD-N1-ZSM-5-1-11-5

TPABr	107
NH ₄ OH	600 cc
F-2000	4.75
LudoxAS-40	442
NaOH	10.8
NiSO ₄ · 6H ₂ O 60 gr	
5.5 Na ₂ O-210(NH ₄) ₂ O-13(TPA) ₂ O-Al ₂ O ₃ -120SiO ₂ -1600H ₂ O-	
9.2NiSO ₄	

DOD-Cu-ZSM-5-1-11-5

TPABr	107
NH ₄ OH	600 cc
F-2000	4.75
LudoxAS-40	442
NaOH	2.16
Cu ²⁺ SO ₄ · 5H ₂ O 1gr (0.2% wt. Cu)	
1 Na ₂ O-13(TPA) ₂ O-210(NH ₄) ₂ O-Al ₂ O ₃ -120SiO ₂ -1550H ₂ O-	
0.16CuSO ₄	

Table 28. Continued

DOD-Pt-ZSM-5-3.6

TPA	107gr
NH ₄ OH	600 cc
F-2000	4.75gr
LudoxAS-40	442gr
NaOH	3.6 gr

H₂PdCl₆ · 6H₂O 87.26 gr of 5 wt% aqueous (0.9 wt% Pt) .

1.8Na₂O - 13(TPA)₂O-210(NH₄)₂O-Al₂O₃-120SiO₂-1600H₂O-
0.34H₂PtCl₆

DOD-Pt-Ins-ZSM-51 (40/1 ZSM-5)

TPA	194 gr
Ludox	343.9 gr
NaAluminate	9.36 gr
NaOH	8.9 gr
H ₂ O	1203 ml

Add (1.8 wt% Pt as H₂PtCl₆ · 6H₂O) in accordance with
incipient wetness

3.6Na₂O - 8.5(TPA)₂O-Al₂O₃-40SiO₂-1872H₂O

DOD-Pd-ZSM-5-2

TPA	107 gr
NH ₄ OH	600 cc
F-2000	4.75 gr
Ludox	442gr
NaOH	2.2 gr

Table 28. Continued

PdCl_2	5.446 gr (1.8wt% Pd)
$1.11\text{Na}_2\text{O}-13(\text{TPA})_2\text{O}-210(\text{NH}_4)_2\text{O}-\text{Al}_2\text{O}_3-120\text{SiO}_2-1550\text{H}_2\text{O}-$	
1.25PdCl_2	
DOD-Pt-ZSM-5-1-11-12	
TPA	107gr
NH_4OH	600 cc
F-2000	4.75gr
LudoxAS-40	442gr
NaOH	4.2gr
$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	87 gr of aqueous solution (0.9 wt% Pt)
5wt% aqueous	
$2.1\text{Na}_2\text{O}-13(\text{TPA})_2\text{O}-210(\text{NH}_4)_2\text{O}-\text{Al}_2\text{O}_3-120\text{SiO}_2-1600\text{H}_2\text{O}-$	
$0.34\text{H}_2\text{PtCl}_6$	
DOD-Ru-ZSM-5-1-11-29	
TPA	107gr
NH_4OH	600cc
F-2000	4.75gr
LudoxAS-40	442gr
NaOH	5.593gr
$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$	23.49 gr (5.2 wt% Ru)
$2.8\text{Na}_2\text{O}-13(\text{TPA})_2\text{O}-210(\text{NH}_4)_2\text{O}-\text{Al}_2\text{O}_3-120\text{SiO}_2-1575\text{H}_2\text{O}-$	
3.7RuCl_3	

Table 28. Continued

DOD-Rh-ZSM-5-2-11-30

TPA	107gr
NH ₄ OH	600cc
F-2000	4.75gr
LudoxAS-40	442gr
NaOH	2.0228gr
RhCl ₃ ·3H ₂ O	2gr (0.44 wt%Rh)

1Na₂O-13(TPA)₂O-210(NH₄)₂O-Al₂O₃-120SiO₂-1575H₂O-
0.31RhCl₃

DOD-Sn-ZSM-5-1-12-30

TPA	214gr
NH ₄ OH	600cc
F-2000	4.75gr
Ludox	442gr
NaOH	2.2gr
SnCl ₄ ·5H ₂ O	5.318 gr (1wt% Sn)

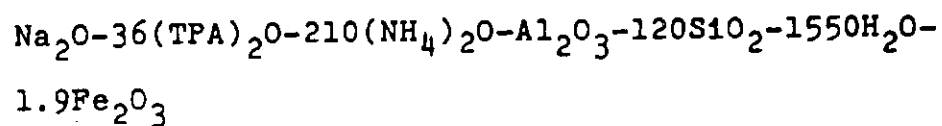
1.11Na₂O-26(TPA)₂O-210(NH₄)₂O-Al₂O₃-120SiO₂-1550H₂O-
0.62SnCl₄

DOD-Fe-ZSM-5-7-12-8

TPA	300gr
NH ₄ OH	600cc
F-2000	4.75gr
Ludox	442gr
Na ₂ O	2.0gr
Fe(OH) ₃	10gr

Table 28. Continued

(2.96 wt% Fe)



DOD-Fe-2

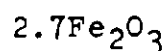
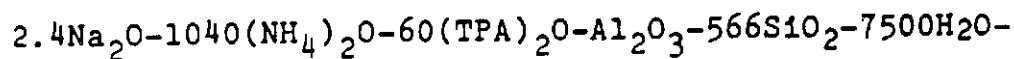
TPABr 213gr

 NH_4OH 1258cc

Reheis F-2000 2.0gr

LudoxAS-40 885gr

NaOH 2.0gr

 $\text{Fe}(\text{OH})_3$ 6.0 gr (1.7wt% Fe)

DOD-Fe-ZSM-5-Br-1

TPABr 103.5gr

 NH_4OH 105cc

LudoxAS-40 221gr

NaOH 1gr

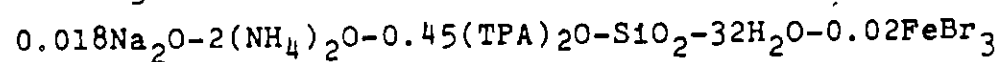
 H_2O 150 FeBr_3 (2% wt Fe)

Table 28. Continued

DOD-Fe-ZSM-5-3

TPABr	107gr
NH ₄ OH	600cc
R-F-2000	1.3gr
LudoxAS-40	442gr
NaOH	1gr
Fe(OH) ₃	30gr (9 wt% Fe)

$1.85\text{Na}_2\text{O}-760(\text{NH}_4)_2\text{O}-46(\text{TPA})_2\text{O}-\text{Al}_2\text{O}_3-435\text{SiO}_2-4900\text{H}_2\text{O}-$
 $21\text{Fe}_2\text{O}_3$

DOD-Pd-ZSM-5-1-115

TPA	107gr
NH ₄ OH	600cc
F-2000	4.75gr
LudoxAS-40	442gr
NaOH	2.0gr

PdCl_2 (5% wt aqueous) 20 gr of 5 wt% aqueous (0.5 wt% Pd)
 $\text{Na}_2\text{O}-13(\text{TPA})_2\text{O}-210(\text{NH}_4)_2\text{O}-\text{Al}_2\text{O}_3-120\text{SiO}_2-1550 \text{H}_2\text{O}-$
 0.23PdCl_2

Table 28, Continued

DOD-Cr-ZSM-5-1-11-12

TPA	107gr
NH ₄ OH	600cc
F-2000	4.75gr
LudoxAs-40	442gr
NaOH	2.48gr
Cr(NO ₃) ₃ ·9H ₂ O	153.6gr (11% wt Cr)
1.25Na ₂ O-13(TPA) ₂ O-210(NH ₄) ₂ O-Al ₂ O ₃ -120SiO ₂ -1650H ₂ O-	
15.5Cr(NO ₃) ₃	

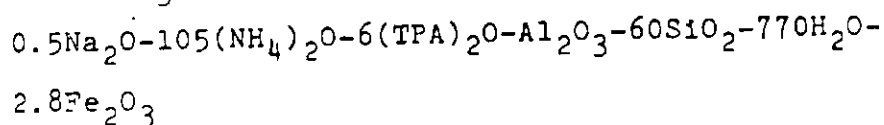
DOD-Ni-ZSM-5-2-11-12

TPA	107gr
NH ₄ OH	600cc
F-2000	4.75gr
LudoxAS-40	442 gr
NaOH	16.27gr
NiSO ₄ ·6H ₂ O	90.4 g (11.3 wt%Ni)
8.2Na ₂ O-13(TPA) ₂ O-210(NH ₄) ₂ O-Al ₂ O ₃ -120SiO ₂ -1600H ₂ O-	
13.8NiSO ₄	

Table 28. Continued

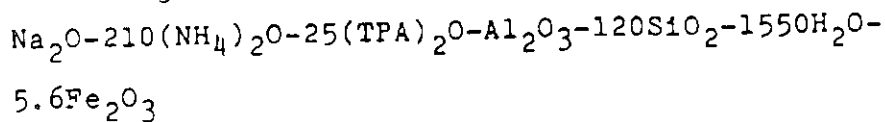
DOD-Fe-ZSM-5-4

TPABr	107gr
NH ₄ OH	600cc
R-F-2000	9.5gr
LudoxAS-40	445gr
NaOH	2.0gr
Fe(OH) ₃	30gr (9wt%Fe)



DOD-Fe-ZSM-5-5

TPABr	214gr
NH ₄ OH	600cc
F-2000	4.75gr
LudoxAS-40	442gr
NaOH	2.0gr
Fe(OH) ₃	30gr (8.7wt %Fe)



DOD-Fe-ZSM-5-6

TPABr	107gr
NH ₄ OH	600cc
R-F-2000	7.5gr
LudoxAs-40	442gr
NaOH	2gr
Fe(OH) ₃	30gr (9wt% Fe)

