Appendix B

DIFRACTION ANALYSIS

Apparatus and Reagents

1. X-ray diffractometer equipped with a strip chart recorder and using
2. Cobolt K-alpha radiation.
3. Drying oven set at $110^{O}C$.
4. Hydrator maintained at 35% relative humidity by a saturated solution of salt, such as $CaCl_2.H_2O$.
5. Planimeter.
6. NaY powder and RE exchanged Y powder.
7. Silicon powder

1. Relative Zeolite Diffraction Intensities

1.1 Procedure

1. Divide the sample finely to permit packing of sample into an XRD sample holder as a self-supporting window.

2. Place about 1.5 g of the sample in the drying oven at $110^{O}C$ for 1 h. Cool the sample in the hydrator and hold at room temperature for at least 16 hr.

3. Obtain a first XRD pattern by scanning over the angle range from 16.27 to 40.87 deg 2θ at 1 deg/min. Figure B-1 shows such a patterns for the reference NaY zeolite.

4. If this first pattern of the sample contains XRD peaks of some nonfaujasite components, it must be established whether this may cause interference in the following steps.

5. Obtain a second XRD pattern by scanning over a small angle range at 0.25 deg/min. The preferred angle range is from 26.2 to 29.1 deg 2θ, the (533) peak.

1.2 Calculation

1.Measure the width of the (533) or alternative peaks obtained from step 5. The width is a measured at half the peak height, that is, half way between the background and the peak maximum.

2. The objective of the method, a value for "XRD intensity/NaY," is obtained in this step. This involves a comparison of the sum of peak heights from the patterns obtained in Step 3.

3. The equation used is the following:

% XRD intensity/NaY = S_X/S_R

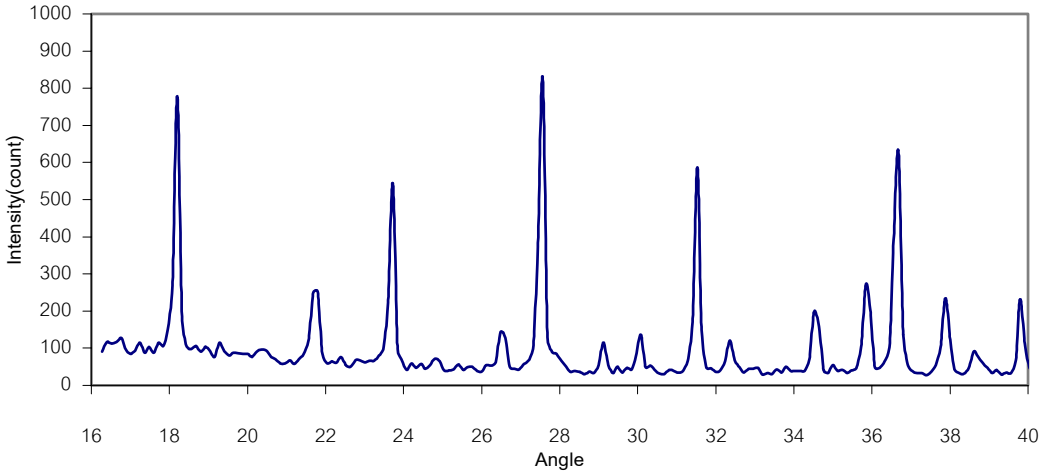
where: S_X = sum of peak heights for the sample and

S_R = sum for the reference NaY.

4. Under certain conditions it may be desirable to base the comparison of zeolite XRD intensity on a single peak rather than on eight peaks. This is the case when the pattern from the sample is very weak so that on the (533) peak, for example, can be measured.

5. Values frequently obtained in Step 2 for the "pure" zeolites listed are given as follows for general guidance:

Zeolites	**%XRD, Intensity/NaY**
NaY, NaX	90 to 105
NH_4Y	100 to 115
REY	25 to 50
USY	80 to 95

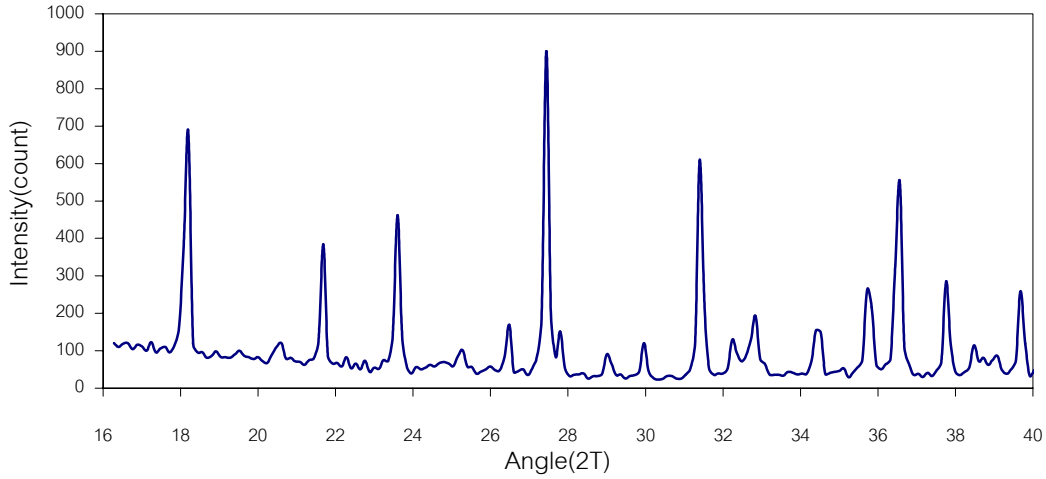


Sample identification: NaY(std)
Start angle [°2q]: 16.280
End angle [°2q]: 40.880
Start d-value[Å]: 6.31731
End d-value[Å]: 2.56133
Maximum number of counts : 841
Anode material : Co
A1 Wavelength [Å] : 1.78897
A2 Wavelength [Å] : 1.79285
Intensities for FIXED slit
Peak positions defined by : Minimum of 2 nd derivative of peak
Minimum peak tip width : 0.00
Maximum peak tip width : 1.00
Maximum peak base width : 2.00
Minimum significance : 0.75
Number of peak: 15

DIFFRACTION LINES :

Angle [°2q]	d-value a1 [Å]	d-value a2 [Å]	T. width [°2q]	Height [count]	Backgr. [count]	Rel. int. [%]	Sinific
18.215	5.65101	5.66328	0.120	718	86	85.4	9.49
21.740	4.74322	4.75352	0.120	342	69	40.7	6.79
23.695	4.35679	4.36626	0.120	488	56	58.1	8.61
26.545	3.96812	3.90459	0.120	149	42	17.7	3.59
27.535	3.75861	3.7667	0.120	841	41	100.0	9.73
30.040	3.45152	3.45901	0.100	114	37	13.6	2.13
31.520	3.29328	3.30043	0.140	552	36	65.7	10.57
32.415	3.20469	3.21165	0.140	102	36	12.12	3.16
34.570	3.01046	3.01700	0.100	222	35	6.4	2.51
35.875	2.90436	2.91067	0.120	339	35	40.3	5.51
36.635	2.84611	2.85229	0.120	713	35	84.8	7.04
37.885	2.75548	2.76147	0.080	202	35	24.0	1.76
38.635	2.70398	2.70985	0.100	72	35	8.6	1.12
39.820	2.62663	2.63234	0.160	196	35	23.3	7.54
40.515	2.58342	2.58903	0.100	106	35	12.6	1.34

Figure B-1 X-Ray diffraction patterns of reference (standard) NaY zeolite.



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Minimum significance : 0.75
Number of peak: 15

DIFFRACTION LINES :

Angle [°2q]	d-value a1 [Å]	d-value a2 [Å]	T. width [°2q]	Height [count]	Backgr. [count]	Rel. int. [%]	Sinific
18.165	5.66643	5.67873	0.080	686	96	71.9	4.39
21.685	4.75511	4.76543	0.080	313	64	32.8	1.24
23.625	4.36952	4.37901	0.100	515	52	54.0	5.85
26.445	3.91059	3.91909	0.120	159	42	16.6	3.67
27.455	3.76935	3.77753	0.120	955	41	100.0	12.28
29.945	3.46222	3.46974	0.120	102	36	10.7	3.00
31.420	3.30350	3.31067	0.120	645	34	67.6	8.95
32.265	3.21919	3.22618	0.120	106	34	11.1	2.63
32.855	3.16293	3.16980	0.140	128	34	13.4	2.74
34.455	3.02020	3.02676	0.100	262	34	27.5	3.06
35.750	2.91418	2.92051	0.080	357	34	37.4	2.18
36.515	2.85514	2.86134	0.100	812	34	85.1	7.05
37.760	2.76427	2.77027	0.080	253	34	26.5	1.99
39.680	2.63552	2.64125	0.100	225	34	23.6	3.20
40.375	2.59200	2.59763	0.100	110	34	11.5	1.92

Figure B-2 Identification of NaY zeolite samples from this work.

An example of the relative crystallinity calculation (the peak 533 method)

At peak 533,

S_X	= (0.12) x (955)	= 114.6
S_R	= (0.12) x (841)	= 100.92
The relative crystallinity	= (114.6)/(100.92)	= 1.136
The sample crystallinity	= (relative crystallinity x % crystallinity of ref.)	
	= (1.136) x $(90)^*$ = 102.24%	

Note: The crystallinity of reference (standard) used is 90%.

Table B-1 Diffraction Angle 2θ hkl Miller Indices (ASTM D3906-80)

Peak	2θ	hkl
1	18.2 ± 0.2	331
2	21.8 ± 0.2	511,333
3	23.7 ± 0.3	440
4	27.6 ± 0.4	533
5	31.6 ± 0.5	642
6	35.9 ± 0.5	822,660
7	36.7 ± 0.5	555,751
8	39.9 ± 0.6	664

2. Determination of the Unit Cell Dimension of a Faujasite-type Zeolite

2.1 Procedure

1. Place 1 g. of powdered catalyst sample the drying oven at 110°C for 1 hr.

2. Blend 1 g. of powered catalyst sample with about 0.05 g. of silicon in a mortar and grind until intimately mixed. Place a thin bed of the mixed sample in the hydrator for at least 16 h. Some samples may be require a longer equilibration time. Pack the hydrated sample in the diffractometer mount

3. Determine the X-ray diffractometer pattern across range from 62 to 71° 2θ

4. Measure the angle of the zeolite reflections at about 62.898° and 68.274° 2θ and that of the 66.218° silicon reflection to at least two decimal places.

Note: when low intensity prevents use of these high-angle reflections, as for example with equilibrium catalysts containing rare earth elements, measure the strong zeolite reflection near 27.356, 31.338 and 36.391 and the silicon reflection at 33.150° 2θ

2.2 Calculation

1.Correct the measured reflection angles for the zeolite by adding the correction factor to each the quantity (Calculated minus measured angle of the silicon reflection). When the silicon reflection of CoKα_1 radiation is measured, the calculated angle is 66.218°.

Note: The corresponding calculated angles when lower angle reflections must be used is 33.150° 2θ (CoKα_1)

2. Convert the corrected angles of reflection to d-spacing values using the equation:

$$D_{hkl} = \lambda/2 \sin\theta$$

Where:

D_{hkl} = distance between reflecting planes having the Miller indices hkl (nm x 10), and

λ = wave length of X-ray radiation which is 1.7889 Å for CoKα_1 Note that the angle used in this calculation is only θ.

3. Calculated the unit cell dimension, of the zeolite in catalyst using the equation

$$\alpha = \{(d_{hkl})^2 (h^2 + k^2 + 1^2)\}^{1/2}$$

Where the sum $(h^2 + k^2 + 1^2)$ of respective zeolite reflections has the following values

Reflection	$(h^2 + k^2 + 1^2)$
68.274°2θ	243
62.898°	211
36.391°	75
31.338°	56
27.356°	43

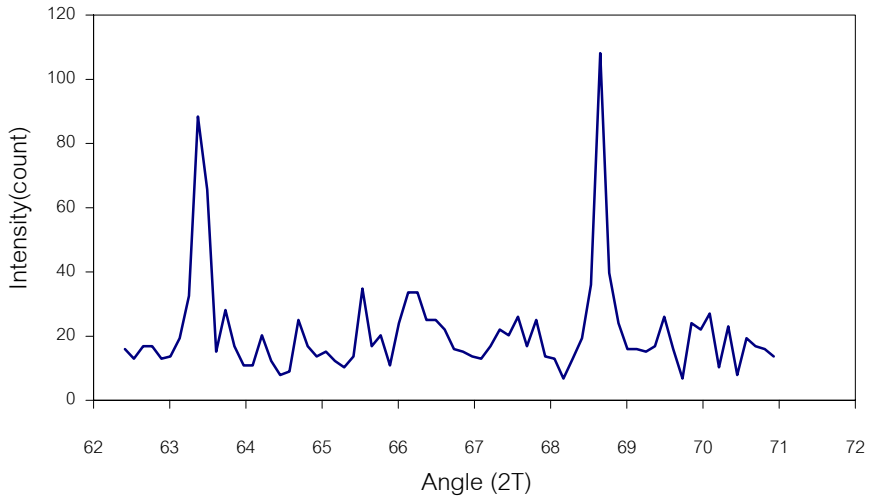
Note: Certain component of a catalyst matrix can interfere with individual peaks. For example, quartz may interfere with the reflection at 31.338° when interference occurs, other reflections should be used in the calculation. Average the valued of α calculated from more than one reflection.

An Example of Unit Cell Size Determination (a sample of NaY)

Calculation

Degrees 2θ			
Measured	***Corrected***	$(h^2 + k^2 + 1^2)$	(α, Å)
63.395	63.423	211	24.72
66.190	66.218	Silicon	-
68.635	68.663	243	24.72
		Average	24.72

Note: the correction factor in the above calculation is {66.218 (standard diffraction angle of Si) – 66.190 (measured diffraction angle of Si) = 0.028°} and is simply added to the measured angle of the two zeolite reflections.



Sample identification: UCS-NaY(PSU)
Start angle [°2q]: 62.410
End angle [°2q]: 70.990
Start d-value[Å]: 1.72646
End d-value[Å]: 1.54053
Maximum number of counts : 83
Anode material : Co
A1 Wavelength [Å] : 1.78897
A2 Wavelength [Å] : 1.79285
Intensities for FIXED slit
Peak positions defined by : Minimum of 2nd derivative of peak
Minimum peak tip width : 0.00
Maximum peak tip width : 1.00
Maximum peak base width : 2.00
Minimum significance : 0.75
Number of peak: 10

DIFFRACTION LINES :

Angle [°2q]	d-value a1 [Å]	d-value a2 [Å]	T. width [°2q]	Height [count]	Backgr. [count]	Rel. int. [%]	Sinific
62.855	1.17544	1.71920	0.320	7	12	8.2	1.07
63.395	1.70237	1.70606	0.080	81	12	97.8	1.92
63.540	1.69889	1.70258	0.060	49	12	59.2	1.17
64.787	1.66969	1.67332	0.240	9	12	10.9	1.12
65.540	1.65257	1.65616	0.120	21	12	25.6	0.97
66.190	1.63816	1.64172	0.320	19	12	23.4	1.45
67.465	1.61076	1.61426	0.480	12	12	14.8	2.67
68.635	1.58659	1.59003	0.808	83	12	100.0	0.86
68.830	1.58264	1.58608	0.100	27	12	32.7	0.75
69.895	1.56153	1.56492	0.120	15	12	18.4	0.87

Figure B-3 Diffraction data of NaY sampled from this work.