Designation: D 3942 – 03

Standard Test Method for Determination of the Unit Cell Dimension of a Faujasite-Type Zeolite[1]

This standard is issued under the fixed designation D 3942; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the unit cell dimension of zeolites having the faujasite crystal structure, including synthetic *Y* and *X* zeolites, their modifications such as the various cation exchange forms, and the dealuminized, decationated, and ultra stable forms of *Y*. These zeolites have cubic symmetry with a unit cell parameter usually within the limits of 24.2 and 25.0 Å (2.42 and 2.50 nm).

1.2 The samples include zeolite preparation in the various forms, and catalysts and adsorbents containing these zeolites. The zeolite may be present in amounts as low as 5 %, such as in a cracking catalyst.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[2]

3. Summary of Test Method

3.1 A sample of the zeolite *Y* or *X*, or catalyst containing zeolite is mixed with powdered silicon. The zeolite unit cell dimension is calculated from the X-ray diffraction pattern of the mixture, using the silicon reflections as a reference.

4. Significance and Use

4.1 Zeolites *Y* and *X*, particularly for catalyst and adsorbent applications, are a major article of manufacture and commerce. Catalysts and adsorbents comprising these zeolites in various forms plus binder and other components have likewise become important. *Y*-based catalysts are used for fluid catalytic cracking (FCC) and hydrocracking of petroleum, while *X*-based adsorbents are used for desiccation, sulfur compound removal, and air separation.

4.2 The unit cell dimension of a freshly synthesized faujasite-type zeolite is a sensitive measure of composition which, among other uses, distinguishes between the two synthetic faujasite-type zeolites, *X* and *Y*. The presence of a matrix in a *Y*-containing catalyst precludes determination of the zeolite framework composition by direct elemental analysis.

4.3 Users of the method should be aware that the correlation between framework composition and unit cell dimension is specific to a given cation form of the zeolite. Steam or thermal treatments, for example, may alter both composition and cation form. The user must therefore determine the correlation that pertains to his zeolite containing samples.[3] In addition, one may use the method solely to determine the unit cell dimension, in which case no correlation is needed.

4.4 Other crystalline components may be present in the sample whose diffraction pattern may cause interference with the selected faujasite-structure diffraction peaks. If there is reason to suspect the presence of such components, then a full diffractometer scan should be obtained and analyzed to select faujasite-structure peaks free of interference.

5. Apparatus

5.1 *X-Ray Diffractometer*, able to scan at 0.25° 2θ/min. 2θ values in the following discussions were based on data obtained with a copper tube, although other tubes such as molybdenum can be used.

NOTE 1—A step-scanning accessory, to scan at a rate of 0.25° or less 2θ/min, will increase the accuracy of the determination and will facilitate measurement in samples of low zeolite content.

5.2 *Drying Oven*, set at 110°C.

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[1] This test method is under the jurisdiction of ASTM Committee D32 on Catalysts and is the direct responsibility of Subcommittee D32.05 on Zeolites.

Current edition approved March 10, 2003. Published April 2003. Originally approved in 1980. Last previous edition approved in 1997 as D 3942–97.

[2] *Annual Book of ASTM Standards*, Vol 14.02.

[3] Three correlations have been published for pure synthetic faujasite-type zeolites in the sodium or calcium form: Breck, D. W. and Flanigen, E. M. in“ Molecular Sieves”, *Society of Chemical Industry*, London, 1968, p. 47, Wright A. C., Rupert, J. P. and Granquist W. T. Amer. Mineral., Vol 53, 1968, p. 1293; and Dempsy, E., Kuehl, G. H., and Olson, D. H., *Journal of the Physical Chemistry*, Vol 73, 1968, p. 387.

5.3 *Hydrator*, maintained at 35 % relative humidity by a saturated solution of salts such as $CaCl_2 \cdot 6H_2O$ maintained at 23°C ± 3°C.

6. Reagents and Materials

6.1 Silicon powder, finely ground or ball-milled to a particle diameter less than 5 µm as determined by microscope. NIST offers a Standard Reference Material (silicon) as an X-ray internal standard (SMR 640) suitable for powder diffraction measurements.

7. Procedure

7.1 Place about 1.5 g of powdered zeolite sample in the drying oven at 110°C for 1 h.

NOTE 2—The drying step eliminates excess water from the sample prior to equilibration at constant-humidity hydration. Most catalyst samples, when received, will not contain excess water. Some sensitive samples may require a lower activation temperature.

7.2 Blend 1 g of powdered zeolite 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 require a longer equilibration time.

7.3 Pack the hydrated sample in the diffractometer mount.

7.4 Determine the X-ray diffraction pattern across the range from 50 to 60° 2θ.

NOTE 3—Smaller slits are desirable for better peak resolution.

NOTE 4—In some catalyst samples, the zeolite reflections at about 53.4° and 57.8° 2θ may be of insufficient intensity for accurate measurement. When this occurs, the diffraction pattern should be determined in the interval 20 to 32° 2θ. Cu Kα consists of the composite of Cu $K\alpha_1$ and Cu $K\alpha_2$. The wavelength for Cu Kα is a weighted average of those of the two components and is appropriate for use only when the components overlap so completely as to show no evidence of existence of more than one diffraction peak. In the frequent case where the resolution is too poor to be certain that the Cu $K\alpha_1$ value should be used but where peak distortion is evident, the value of peak location is taken as the midpoint at one-quarter peak height, measured from the base up, and the wavelength for Cu Kα is used.

NOTE 5—If the instrument software has the ability to remove the Cu $K\alpha_2$ contribution, it should be used when employing the low angle reflections (in the 20 to 32° range).

7.5 Measure the angle of the zeolite reflections at about 53.4° and 57.8° 2θ and that of the 56.1° silicon reflection to at least two decimal places. For noncomputerized systems, if both the two Cu $K\alpha_1$ and Cu $K\alpha_2$ reflections are clearly apparent, measure the angle of reflection peak (Cu $K\alpha_1$) as the midpoint at ¾ peak height.

NOTE 6—When low intensity prevents use of these high-angle reflections, as for example with equilibrium catalysts containing rare earth elements, measure the strong zeolite reflections near 23.5°, 26.9°, and 31.2° and the silicon reflection at 28.5° 2θ (Cu Kα).

8. Calculation

8.1 Correct the measured reflection angles for the zeolite by adding to each the quantity (calculated minus measured angle of the silicon reflection). When the silicon reflection of Cu $K\alpha_1$ radiation is measured, the calculated angle is 56.123° 2θ; with Cu Kα, the calculated angle is 56.173° 2θ.

NOTE 7—The corresponding calculated angles when lower angle reflections must be used are 28.443° 2θ (Cu $K\alpha_1$) and 28.467° 2θ (Cu Kα).

8.2 Convert the corrected angles of reflection to *d*-spacing values using the equation:

$$d_{hkl} = \frac{\lambda}{2 \sin \theta} \tag{1}$$

where:

d_{hkl} = distance between reflecting planes having the Miller indices *hkl*, Å(nm × 10), and

λ = wavelength of X-ray radiation which is 1.54178 Å (0.154178 nm) for Cu Kα and 1.54060 Å (0.154060 nm) for Cu $K\alpha_1$. Note that the angle of reflection measured from the X-ray diffraction pattern is 2θ, while the angle used in this calculation is only θ.[4]

8.3 Calculate the unit cell dimension, *a*, of the zeolite using the equation:

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

where the sum $(h^2 + k^2 + l^2)$ of the respective zeolite reflections has the following values:[5]

Reflection	$(h^2 + k^2 + l^2)$
57.8° 2θ	243
53.4°	211
31.2°	75
26.9°	56
23.5°	43

NOTE 8—Certain components of a catalyst matrix can interfere with individual peaks. For example, quartz may interfere with the reflection at 26.9°. When an interference occurs, other reflections should be used in the calculation.

8.4 Average the values of *a* calculated from more than one reflection.

8.5 An example of a determination can be shown from the X-ray diffraction pattern of a NaY sample, Fig. 1. Cu $K\alpha_1$(peak) and Cu $K\alpha_2$(shoulder) are readily apparent on all three designated reflections, so that Cu $K\alpha_1$ values will be used in the calculation. The angle of the peak of the reflection is measured as follows:

Degrees 2θ			
Measured	Corrected	$(h^2 + k^2 + l^2)$	(a, Å)
58.197	58.215	243	24.683
56.105	56.123	silicon	—
53.872	53.890	211	24.691
			24.687 average

The correction factor in the above calculation is {56.123 (calculated for Si) − 56.105 (measured) = 0.018°} and is simply added to the measured angle of the two zeolite reflections. A *d*-spacing value for each of these two reflections is obtained from the standard Cu $K\alpha_1$ tables (8.2) and values of the unit cell dimension, *a*, are then calculated according to the equation in 8.3.[6]

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[4] Conversion tables exist and are commonly used for calculating d-spacings. For example, see Fang, J. H. and Bloss, F. D., *X-Ray Diffraction Tables*, Southern Illinois University Press, Carbondale, IL. 1966.

[5] For a complete listing of *hkl* values in the range, 5 to 55° 2θ, see Broussard, L. and Shoemaker, D. P., *Journal of the American Chemical Society*, Vol 82, 1960, p. 1041.

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D32–1002.

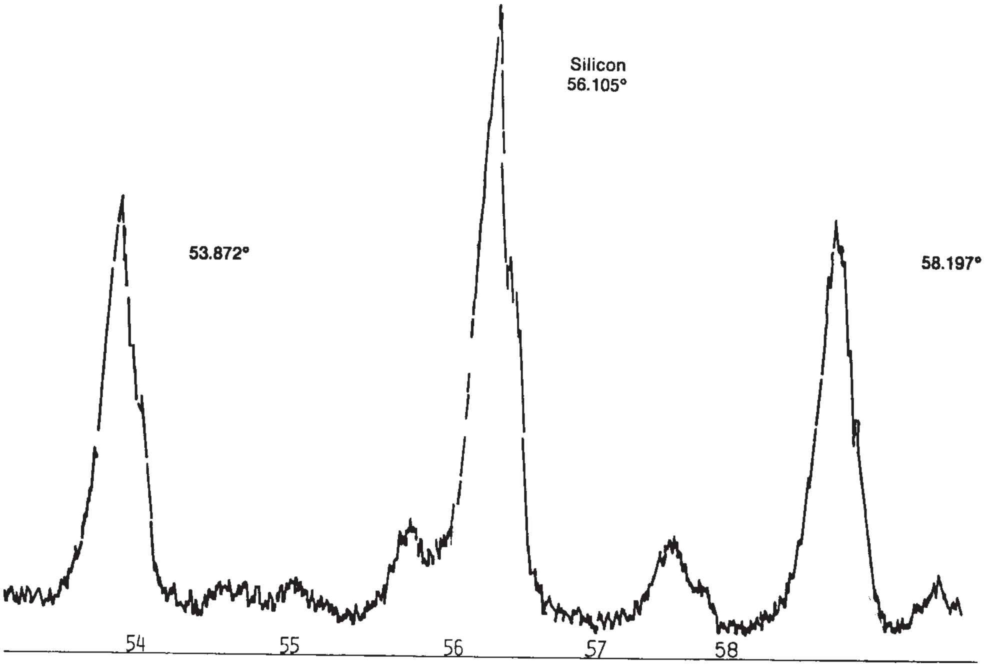

FIG. 1 X-Ray Diffraction Pattern of NaY

9. Report

9.1 Report the following information.

9.1.1 Unit cell dimension, *a*, in Angstroms. (10 Angstroms = 1 nm.)

9.1.2 The reflections used in the calculation.

10. Precision and Bias

10.1 *Test Program*—An interlaboratory study was conducted in which nine laboratories participated. Practice E 691 was used for data reduction. Details are in the research report.

10.2 The following criteria should be used for judging the acceptability of the results:

10.2.1 *Repeatability*—Duplicate results by the same operator should be considered suspect if they differ by more than 0.02Å (0.002 nm).

10.2.2 *Reproducibility*—The results by each of two laboratories should be considered suspect if they differ by more than 0.04 Å (0.004 nm).

10.3 *Bias*—Since an accepted value is not available, the bias has not been determined.

11. Keywords

11.1 catalyst; faujasite; unit cell; X-ray diffraction; zeolite

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