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Standard Test Method for Determination of Relative Crystallinity of Zeolite ZSM-5 by X-Ray Diffraction[1]

This standard is issued under the fixed designation D5758; 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 a procedure for determination of the relative crystallinity of zeolite ZSM-5 using selected peaks from the X-ray diffraction pattern of the zeolite.

1.2 The test method provides a number that is the ratio of intensity of a portion of the XRD pattern of the sample ZSM-5 to intensity of the corresponding portion of the pattern of a reference ZSM-5. The intensity ratio, expressed as a percentage, is then labeled percent XRD relative crystallinity/ZSM-5. This type of comparison is commonly used in zeolite technology and is often referred to as percent crystallinity.

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:*[2]

D3906 Test Method for Determination of Relative X-ray Diffraction Intensities of Faujasite-Type Zeolite-Containing Materials
D5357 Test Method for Determination of Relative Crystallinity of Zeolite Sodium A by X-ray Diffraction
E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E456 Terminology Relating to Quality and Statistics
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Summary of Test Method

3.1 XRD patterns of the sample ZSM-5 and the reference ZSM-5 are obtained under the same conditions. From these patterns, there is a choice from two procedures for calculation of relative crystallinity/ZSM-5.

3.1.1 *Procedure A (Integrated Peak Area Method)*—A comparison is made of the sums of intensities (sample versus reference) of the strong peaks, having maxima between about 23.1 and 24.3° 2θ.

3.1.2 *Procedure B (Peak Height Method)*—A comparison is made of the absolute peak heights (sample versus reference) of the 24.3° 2θ peak.

4. Significance and Use

4.1 ZSM-5 is a siliceous zeolite that can be crystallized with SiO_2/Al_2O_3 ratio in the range of 20 to greater than 1000. ZSM-5, upon modification to the H-cation form (HZSM-5) in a post-crystallization step, has been used since the 1970s as a shape selective, acid-site catalyst for petroleum refining and petrochemicals production, including such processes as alkylation, isomerization, fluid cracking catalysis (FCC), and methanol-to-gasoline. The most siliceous member of the ZSM-5 family, sometimes called silicalite, is hydrophobic and it is used for selective sorption of organic molecules from water-containing systems.

4.2 This X-ray procedure is designed to allow a reporting of the relative degree of crystallization upon manufacture of ZSM-5. The relative crystallinity/ZSM-5 number has proven useful in technology, research, and specifications.

4.3 The Integrated Peak Area Method (Procedure A) is preferred over the Peak Height Method (Procedure B) since it calculates XRD intensity as a sum from several peaks rather than utilizing just one peak. Drastic changes in intensity of individual peaks in the XRD pattern of ZSM-5 can result from changes in distribution of electron density within the unit cell of the ZSM-5 zeolite. The electron density distribution is dependent upon the following factors:

4.3.1 Extent of filling of pores with guest molecules and the nature of these guest molecules.

4.3.2 Type of cations and extent of their presence (these cations may also affect the absorption of X rays by the ZSM-5 sample).

4.3.3 In this XRD method, the guest molecule H_2O completes the filling of the pores. Other guest molecule types may also be present, including one of numerous amines, diamines,

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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.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

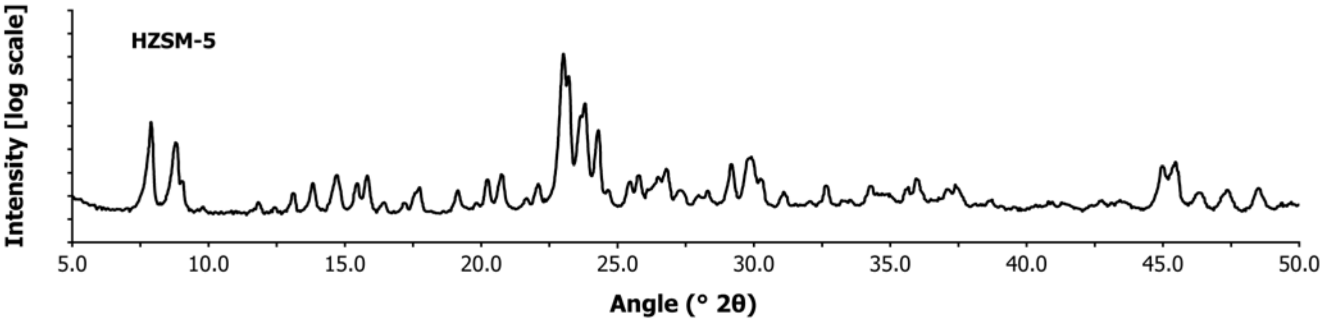

FIG. 1 X-Ray Diffraction Wide Scan Pattern of Zeolite ZSM-5—ASTM Z-20 (Reference)

and quarternary ammonium cations that can function as a template for crystallization of the ZSM-5 structure.

4.3.4 Because of the factors mentioned in 4.3.1 to 4.3.3 that could vary the intensities of the XRD peaks in ZSM-5, this XRD method will provide the best determination of relative crystallinity when the reference ZSM-5 and sample ZSM-5 have a similar history of preparation and composition.

4.4 ZSM-5 can exist with either orthorhombic or monoclinic symmetry, depending upon the composition of the precursor gel or post-crystallization modification conditions, or both. In the orthorhombic type, the XRD peaks centered at about 23.1 and 23.8° 2θ are usually split into doublets, whereas the less symmetric monoclinic type may show a further split of these peaks into triplets. The peak area intensities of these peaks are unaffected by the crystalline form. The XRD peak at 24.3° 2θ for the orthorhombic form is a singlet and hence is the most suitable for the Peak Height Method (Procedure B). If the 24.3° peak is split (doublet in the monoclinic form), then the Integrated Peak Area Method (Procedure A) should be used.

4.5 If crystalline phases other than ZSM-5 are present in the sample, their diffraction peaks may overlap with some of the ZSM-5 peaks selected for the Integrated Peak Area Method (Procedure A). If there is reason to suspect the presence of such components, then the Peak Height Method (Procedure B) should be chosen for analysis provided that there is no interference with the 24.3° 2θ peak that is used for the calculation.

5. Apparatus

5.1 *X-ray Diffractometer,* equipped with computerized data acquisition and reduction capability, or with a strip chart recorder, and using copper K-alpha radiation.

5.2 *Drying Oven,* set at 105 ± 5°C.

5.3 *Hydrator (Laboratory Desiccator),* maintained at about 58 % relative humidity by a saturated solution of sodium bromide, NaBr.

5.4 *Planimeter.*

NOTE 1—The planimeter will not be needed if the XRD instrument is equipped with computerized data acquisition and reduction capability.

6. Reagents and Materials

6.1 *ZSM-5 Powder,* [3] as reference standard, preferably with a mean particle diameter of less than 10 µm.

7. Procedure

7.1 Carry out steps 7.2 through 7.4, in an identical manner, for both the sample ZSM-5 and the reference ZSM-5.

7.2 Place about 1.5 g of finely divided ZSM-5 in the drying oven at 105°C for 2 h. Cool the sample in the hydrator and hold there at room temperature and about 58 % relative humidity for at least 16 h.

NOTE 2—Grinding of course-textured samples should be done gently. Overgrinding can lead to breaking up of fine crystals and destruction of the zeolite.

NOTE 3—Drying, followed by rehydration, results in filling the zeolite pores with water of hydration but without an excess of moisture residing on the surface of the zeolite particles.

7.3 Pack the humidity-conditioned sample into an XRD sample holder.

7.4 Obtain an XRD pattern of the reference ZSM-5 and also obtain a pattern of the sample ZSM-5 (in the same day), by scanning over the angle range from 11 to 32° 2θ using instrument parameters best suited to the X-ray diffractometer. The scan rate should not be greater than 1.0°/min. The scan range includes the diffraction peaks that are to be used in the calculation for relative crystallinity. The XRD pattern of the sample can also be used to check for crystalline phases other than ZSM-5 that might be present and might interfere with the utility of the calculation of Procedure A (see 4.5). Fig. 1 shows a pattern for the reference ZSM-5 (H^+ cation form) used in the testing of this test method.

7.4.1 If a strip chart recorder is used, set the chart drive at 20 mm/min. Select the scale factor (for amplification) for the reference ZSM-5 pattern so that the strongest peak at 23.1° 2θ is between 50 and 100 % of full scale. The same scale factor should be used for the sample ZSM-5 pattern. However, if the sample gives considerably lower peak intensities, the scale factor may be reduced (amplification increased) in order to provide reasonable peak heights.

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[3] Available from NIST as RM8852.

8. Calculation

8.1 *Procedure A (Integrated Peak Area Method)*—This calculation involves a comparison of the integrated peak areas in the range of 22.5 to 25.0° 2θ (measured above background) from the patterns obtained in 7.4.

8.1.1 Obtain an integrated peak area encompassing the three to five strong peaks in the 22.5 to 25.0° 2θ range for both the sample ZSM-5 and the reference ZSM-5. The area is generally determined in one of two ways:

8.1.1.1 From the counts recorded by a digital integrating system that is used while obtaining the pattern.

8.1.1.2 By measuring the area under the peaks with a planimeter.

8.1.2 Calculate the relative crystallinity using the equation:

$$\% \text{ XRD relative crystallinity ZSM-5} = \frac{S_x}{S_r} \times 100 \quad (1)$$

where:

S_x = integrated peak area for the sample ZSM-5, and
S_r = integrated peak area for the reference ZSM-5.

8.2 *Procedure B (Peak Height Method)*—This calculation involves a comparison of the peak heights at 24.3° 2θ (measured above background) from the patterns obtained in 7.4.

8.2.1 Construct a baseline from the center of the background scatter at 21.2° 2θ to the center of the background scatter at 25.0° 2θ on the XRD patterns (hardcopy or stripchart) of the sample ZSM-5 and reference ZSM-5. Determine the absolute heights of the respective peaks centered at 24.3° 2θ; that is, measure the height, in millimetres, from the baseline to the apex of the peak. Fig. 2 shows an example of the peak height determination.

8.2.2 Calculate the relative crystallinity using the equation:

$$\% \text{ XRD relative crystallinity ZSM-5} = \frac{H_s}{H_r} \times 100 \quad (2)$$

where:

H_s = peak height for the sample, and
H_r = peak height for the reference.

NOTE 4—Peak area or peak heights determined by the techniques in 8.1.1.2 or 8.2.1 must be obtained from XRD patterns that have a linear intensity scale, and must have a correction factor applied if the scale factors used for the ZSM-5 reference and sample patterns are different; see Test Method D3906 and D5357.

NOTE 5—Some samples of zeolite may be slightly more crystalline than a chosen reference material. Thus relative crystallinity values greater than 100 % may be obtained.

NOTE 6—Peak broadening in XRD patterns of zeolites can occur for a variety of reasons, including small crystal size (below about 0.2 µm), disorder, absorption, and inconsistent sample packing density. ZSM-5 products can be manufactured having a wide range of mean crystal sizes, including less than 0.2 µm. Thus the percent XRD relative crystallinity of the small crystal ZSM-5, when calculated by the Peak Height Method (Procedure B), may be erroneously low.

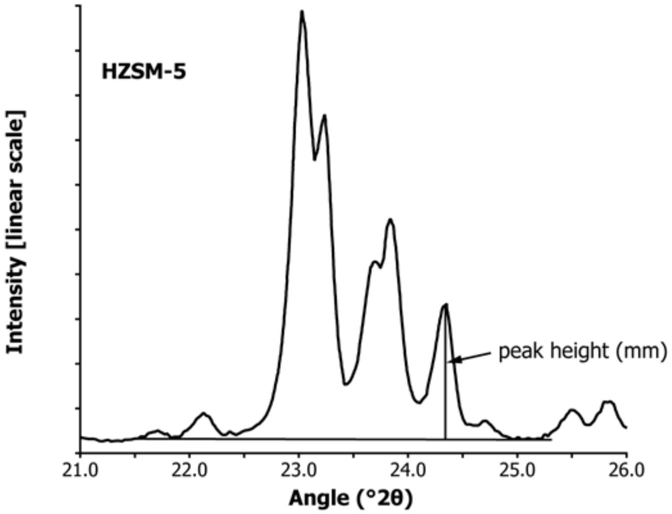

FIG. 2 X-Ray Diffraction Short Scan Pattern of Zeolite ZSM-5—ASTM Z-20 (Reference) (for Peak Height Method—Procedure B)

9. Report

9.1 *Report the following information:*

9.1.1 Relative crystallinity of ZSM-5,

9.1.2 The utilized procedure, that is, the Integrated Peak Area Method or the Peak Height Method, and

9.1.3 Non-ZSM-5 peaks, if present (impurity identificaiton, if possible).

10. Precision and Bias

10.1 *Test Program*—An interlaboratory study was conducted in which the named property was measured in two separate test materials in ten separate laboratories. Practice E691, modified for non-uniform data sets, was followed for the data reduction. Analysis details are in the Research Report.

10.2 *Precision—*Pairs of test results obtained by a procedure similar to that described in the study are expected to differ in absolute value by less than 2.772 × S, where 2.772 × S is the 95 % probability interval limit on the difference between two test results, and S is the appropriate estimate of standard deviation. Definitions and usage are given in Practices E456 and E177, respectively. See Table 1.

10.3 *Bias*—This test method is without known bias.

11. Keywords

11.1 crystallinity; X-ray diffraction; zeolite ZSM-5

TABLE 1 Precision Data

Calculation Procedure	Test Result (consensus mean)	95 % Repeatability Interval (within laboratory)	95 % Reproducibility Interval (between laboratories)
Integrated peak area	95.62 %	2.19 % (2.29 % of mean)	5.04 % (5.27 % of mean)
Peak height	91.11 %	5.33 % (5.84 % of mean)	10.42 % (11.44 % of mean)

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