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Mechanical Strength of Solid Catalysts: Recent Developments and Future Prospects

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DOI 10.1002/aic.11291
Published online August 31, 2007 in Wiley InterScience (www.interscience.wiley.com).

Mechanical strength of solid catalysts is one of the most important factors for the reliable and efficient performance of a reactor. Some recent developments on the basic mechanics of solid catalysts are reviewed in this article. The main concepts discussed are the brittle fracture which leads to the mechanical failure of the catalyst pellets, the measurement and statistical properties of the catalyst strength data, the mechanical reliability of the catalyst pellets, the mechanical properties of the catalyst packed beds, etc. For the purpose of an integrated research on catalyst mechanical properties, a multi-scale framework for the mechanics of the fixed bed catalysts is also proposed. The scientific basis for the issues on the catalyst mechanical properties calls yet for further elucidation and advancement. © 2007 American Institute of Chemical Engineers *AIChE J,* 53: 2618–2629, 2007

Keywords: solid catalysts, mechanical strength, reliability, Weibull statistics, fixed bed reactor

Introduction

Solid catalysts are normally agglomerates of mixed metal oxides, or supported metal, metal oxide, and sulphide on high-melting oxide agglomerates. They are brittle materials fabricated deliberately to produce high porosity and optimized pore distribution. Commercial catalysts have a wide spectrum of shapes, e.g., spheres, tablets, extrudates, rings, granules, etc.

It is well known that a successful solid catalyst requires not only good catalytic properties such as selectivity and activity, but also good physical properties such as mechanical strength.[1,2] Catalyst pellets may experience various damaging stresses, e.g. thermal, chemical, and mechanical stresses, in the reactors or during transport and storage, as shown in Figure 1. Mechanical failure of the catalyst pellets results in the formation of fragments and fines, which can cause various problems for the running of industrial units.[3–6] For example, the formation of fragments and fines can lead to maldistribution of fluid flow, blockage, and unacceptably high pressure drop across the reactor, variations in heat flux, downstream fouling, and in some cases to environmental problems because of the release of fines into the atmosphere. The mechanical strength of solid catalysts is therefore one of the key parameters for the reliable and efficient performance of an industrial reactor.[7–10] However, academic institutions active in catalysis research generally concentrate on the chemistry rather than the mechanical properties of catalysts. Few articles on the catalyst strength are therefore available in the open literature. Because of insufficient involvement of academe, it is reasonable that in many industrial applications the mechanical or physical failure of the catalyst pellets is more often the cause of process shutdowns and catalyst replacements than their loss of catalytic activity, as Beaver[3,4] remarked.

This article aims to provide an insight into some aspects of the catalyst strength and to propose future prospects of the research on the mechanical properties of solid catalysts. It

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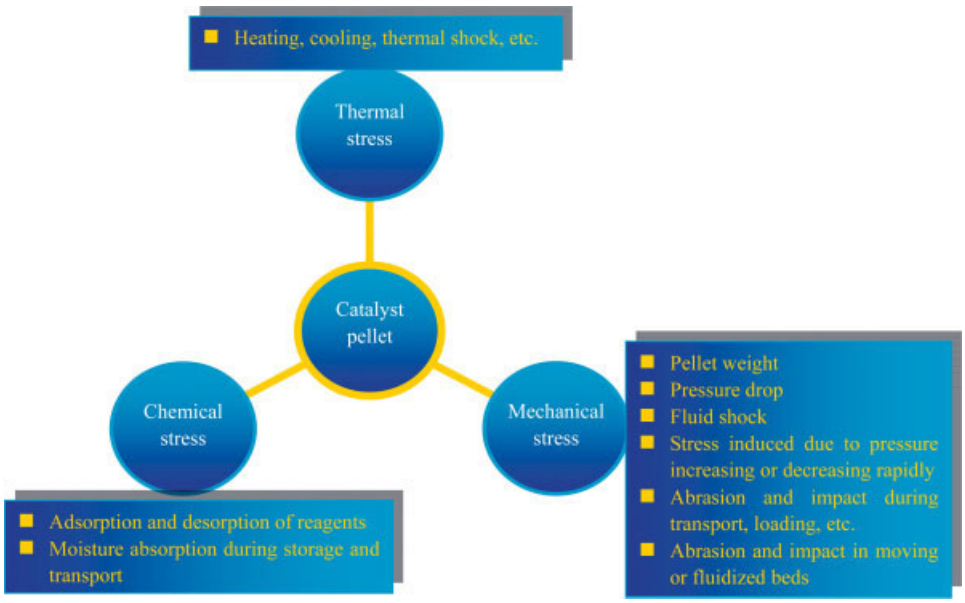

Figure 1. Various stresses that the catalyst pellets may experience.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

will focus on catalyst pellets in fixed bed reactors, and problems such as attrition in fluidized and moving bed reactors are not covered, these have been introduced previously by Bemrose and Bridgwater.[11]

Mechanical Failure of Catalyst Pellets

Solid catalysts are fragile.[1,12] Textbook chapters and some articles on catalyst engineering give good guidelines for catalyst handling: do not drop; do not roll the drum which contains a catalyst; do not drop the pellets into a reactor, and fill the reactor with a great care; do not heat a catalyst with a high heating rate, and keep a catalyst from moisture.

It has been shown that mixed oxides and oxide-supported metal catalysts are typical materials with a brittle failure mode and that their mechanical failure is due to brittle fracture.[13–16] The load–displacement curve during the crushing strength test of the catalyst pellets, as illustrated in Figure 2, shows that the pellets experience very little plastic deformation and a small elastic deformation before the fracture happens. Part of the elastic strain energy accumulated in the specimen during the diametral compression is used to create new surfaces of the fragments, which leads to the fact that the fracture section is greatly unsmoothed and has complicated striae,[17] as shown in Figures 3A and B. On the other hand, the remaining energy is transformed into kinetic energy, which makes the fragments tend to fly away after the fracture.[18] Another reason for the ejection of the fragments is the reflection of the compressive wave as a tensile wave at the free surface, which was analytically calculated and experimentally measured by Bajons and Peterlik[19] for glass as a model material. The pellets breaking at small loads will tend to form a small number of fragments (typically two hemispheres for a spherical pellet and two half particles along the plane passing through the two loading lines for a tablet), whereas the pellets breaking at higher loads will tend to break into a larger number of segments. We also examined the catalyst pellets which failed in several commercial reactors, as shown typically in Figure 3C for the fragments formed through brittle fracture.[14] Furthermore, the data of the catalyst mechanical strength scatter in a broad range, and the fracture of the catalyst pellets when subjected to a critical load occurs very fast.[13–16,20] All of these are characteristics of solid materials with a brittle failure mode.

As a force is loaded on a material, a tensile stress field is induced inside the material bulk.[21,22] Brittle fracture of the material originates from tensile stress concentration at the tips of an existing critical micro-crack (flaw) inside the mate-

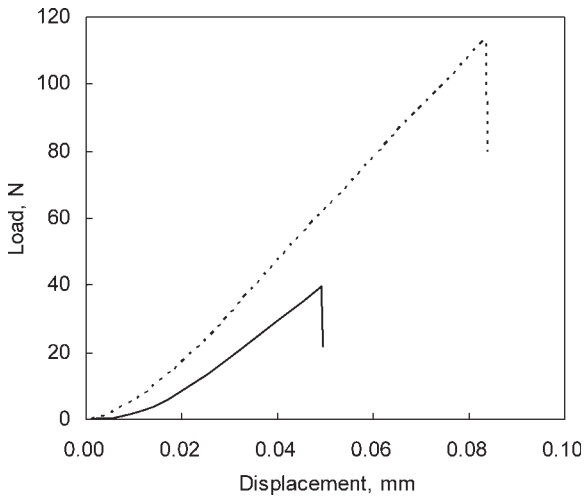

Figure 2. Typical load-displacement curves during the crushing strength tests of two catalyst pellets. (Solid line) a spherical Al_2O_3; (Dashed line) a tablet.

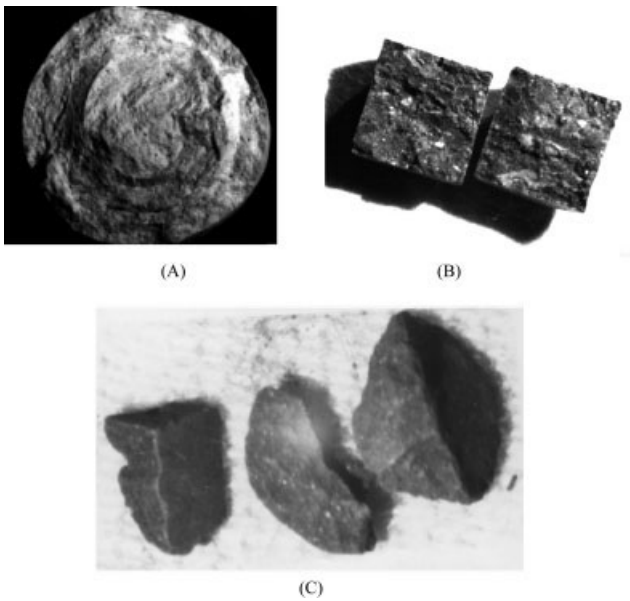

Figure 3. Fracture pieces in different cases. Pieces of a spherical pellet (A) and a tablet (B) after their crushing strength tests, and pieces selected from a failed commercial catalyst (C) after industrial application.

rial bulk, which leads to a sudden catastrophic growth of the critical flaw under tensile stress.[17] Solid catalysts are porous and full of defects, crystal edges, dislocations or nonidentical materials enclosed, e.g., graphite and other additives. Any discontinuity that appears in the catalyst bulk may be treated as a flaw and hence as the origin of tensile stress concentration. The Griffith equation relates the fracture stress σ_f to the inverse square root of crack length.[17]

$$\sigma_f = \sqrt{\frac{2E\gamma}{\pi c}} \tag{1}$$

where E is modulus of elasticity, also called Young's modulus, and γ is specific surface energy, i.e. the energy required to create a unit area of new crack surface, and c the crack half-length. Clearly, the fracture strength of brittle materials such as solid catalysts has a close relationship with the flaw properties in the materials.

Measurement of the Mechanical Strength of Catalyst Pellets

Since the first academic event on the standardization of catalyst characterization was held in 1974 in the United States,[3,4,23–26] the methodology for the mechanical strength measurement of solid catalysts has been a topic of the annual meetings of ASTM committee D32 on catalysts, as shown on the ASTM website, www.astm.org.

Couroyer et al.[8] developed a method for the characterization of the mechanical strength of reforming catalyst pellets in order to reproduce the same type and range of the mechanical stresses experienced by the pellets in the industrial units. It includes the measurements of material properties such as modulus of elasticity, hardness and fracture toughness, single pellet crushing and impact tests and bulk pellet crushing, and shearing tests. However, in industry, the main mechanical test used for catalyst pellets is still a single pellet crushing strength test, as it can be easily set up in any laboratory and allows a quick measurement of the crushing loads of the sample. The crushing test consists of the slow deformation of individual pellets by a platen moving against a static platen until the pellet fracture and a characteristic drop of the crushing load (see Figure 2). The maximum applied force before the pellet fracture is recorded as the crushing strength. Hutchings[27] suggested that the crushing strength of catalyst pellets could be used as a diagnostic test for catalyst mechanical strength. The single pellet crushing strength measurement has, therefore, been accepted as a standard method in many countries.[28–31] For example, in the ASTM standards, the radial crushing strength is used for the characterization of catalyst pellets of various shapes, e.g., tablets, spheres, and extrudates. The number of the pellets that needs to be tested for a catalyst sample is 50–200, depending on the precision required and the homogeneity of the material being tested. Moreover, a mean value and standard deviation of the measured strength data are recommended by ASTM for the report of the results.

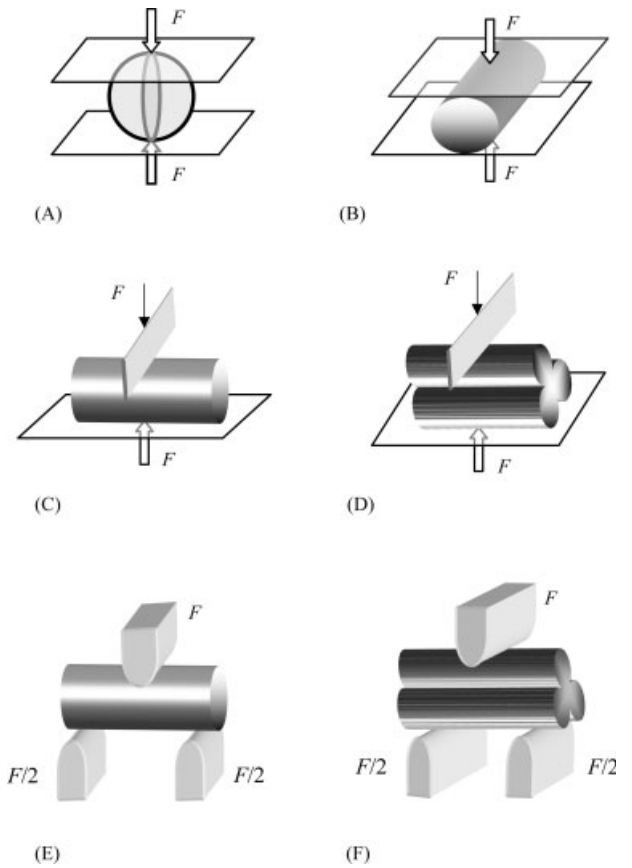

Figure 4. Schematic diagrams of various indirect tensile strength tests.

(A) Spherical pellet in crushing; (B) cylindrical pellet in crushing; (C) cylindrical pellet in cutting; (D) trilobite pellet in cutting; (E) cylindrical pellet in bending; (F) trilobite pellet in bending.

Table 1. Statistics of the Crushing Strength Data of Six Commercial High-Temperature Water-Gas Shift Catalysts

	Nominal Size, mm		Radial Crushing Strength Measured, kg/tablet					Weibull Parameters		Fracture Load with Specific Probabilities of Failure, kg/tablet		
No	Diameter	Height	Mean	Standard Deviation	Minimum	Maximum	Max-Min	m	F_0, kg/tablet	1%	5%	10%
1	9.1	5.17	27.5	8.64	9.50	48.3	38.8	3.58	30.5	8.46	13.3	16.3
2	9.1	6.59	34.2	11.2	12.9	66.9	54.0	3.41	38.0	9.87	15.9	19.7
3	9.6	4.79	30.0	5.25	18.0	40.2	22.2	6.45	32.2	15.8	20.3	22.7
4	9.6	4.91	23.3	4.38	14.9	36.0	21.1	6.22	25.0	11.9	15.5	17.4
5	5.4	3.6	17.3	6.48	3.40	30.0	26.6	2.31	19.9	2.71	5.49	7.50
6	6.0	6.0	17.1	5.17	8.80	29.7	20.9	3.70	18.9	5.46	8.48	10.3

Samples 1–4 are plane-faced tablets, and 5, 6 are double convex-faced tablets.

Extruded pellets of catalyst are often fabricated as cylinders, multilobes, and tubes. In commercial practice, a material is extruded as pastes of enough plasticity.[32] Extrusion is followed by cutting and conveying before heat treating. As the green pellets are plastic, deformation and curvature are often found for the formed pellets. For pellets with irregularities, radial crushing measurement of strength is doubtful, because of the nonrepeatability of stress distribution for different specimens within one sample.[15] Repeatability of stress distribution during measurement is one of the key prerequisites for obtaining correct results. Therefore, we proposed to use different methods to measure the mechanical strength of differently shaped catalyst pellets, as summarized in Figure 4. Correlation of the real strength data of differently shaped catalysts and theoretical analysis support the proposal. For instance, the crushing strength method is suitable for spheres and tablets or other short regular cylinders, while the bending method is appropriate to extrudates with a comparatively large ratio of length to diameter, and the cutting method well fits tablets and extrudates with more irregularities.[15]

The measurement of the single pellet strength allows a possible comparison of the catalyst mechanical properties among various samples. However, it should be noted that some parameters such as the pellet size, loading mode, loading speed, loading platens material properties, temperature, and humidity of the sample may have direct effects on the measured strength data. Therefore, caution should be exercised when comparing samples tested in different laboratories or with different equipment.

Statistical Properties of the Mechanical Strength

It has been shown that the mechanical strength of solid catalysts is always distributed over a wide spread of values, even if a set of nominally identical specimens, taken from a batch of catalysts, are tested under the same conditions.[13–16,20] For most industrial catalysts, differences between the maximum and minimum values of the strength data are larger than the mean strength of the corresponding samples, as illustrated in Table 1.[14] There exist large numbers of various flaws inside the catalyst bulk. Griffith equation, i.e. Eq. 1 shows that variations of size, shape, and orientation of these flaws result in a large scatter of the strength data of solid catalysts. Thus it can be seen that the heterogeneity of the catalyst strength is an intrinsic property inherited from the brittle fracture nature of the mechanical failure of solid catalyst materials.

Such a large variation in the strength data makes the report of the measurement according to the standards,[28–31] i.e., the mean value and standard deviation of the data, uninformative. For the comparison of the mechanical strength between different samples, it cannot be concluded that one sample which has the highest mean strength, would have the best mechanical property, taking into account the variation. However, if a probability distribution is correctly chosen to describe the mechanical strength, the distribution can be used to predict the probability of failure of the catalyst pellets at a specific load or the fracture load with a specific probability of failure. This information, obtained from the probability distribution, is useful for determining the mechanical reliability of the catalyst pellets and comparing the mechanical properties between different catalyst samples. The ability to predict the mechanical strength variation by a suitable theoretical distribution is also necessary for catalyst manufacturers to plan production processes and to develop control strategies, etc. Therefore, the catalyst strength is not a well-defined quantity and has to be described with a statistical approach.

It was concluded by van den Born et al.[33] that the Duxbury-Leath distribution appears to be appropriate to describing the mechanical strength of highly porous ceramic catalyst pellets. In the standard of ASTM D 4179-01,[28] the catalyst pellet crushing strength is assumed to follow a normal distribution. Li et al.[13–15] and Subero-Couroyer et al.[16] suggested that the mechanical strength of the catalyst pellets with a brittle failure mode could be adequately represented with a Weibull distribution. Recently, a rigorous analysis has been made to fit the measured strength data of the catalyst pellets to normal, lognormal, and Weibull distributions and to check the suitability of these model distributions to the experimental data.[20] It was concluded that the Weibull distribution can always represent the catalyst strength data very well, though sometimes it may not be the optimal candidate. Nevertheless, the normal and lognormal distributions are both not universal models for the mechanical strength variation.

It is well known that Weibull statistics has been widely used to characterize the statistical variation in the fracture strength of brittle materials such as ceramics, fibers, and glasses.[34–37] It is based on a "weakest link theory," which means that the most serious flaw in the material will control the strength, like a chain breaking if the weakest link fails. The most serious flaw is not necessarily the largest one

because its severity also relies on its location and orientation. In other words, the flaw subjected to the highest stress intensity factor will be strength controlling.

The three-parameter Weibull distribution is given by[38]

$$P = 1 - \exp\left[-\frac{1}{V_0}\int\left(\frac{\sigma - \sigma_u}{\sigma_0}\right)^m dV\right] \quad (\sigma \geq \sigma_u) \tag{2}$$

where P is the probability of failure at a tensile stress σ induced in the specimen, V the specimen volume where the stress exists, V_0 the unit volume, σ_0 the scale parameter, σ_u the location parameter, also called the threshold stress below which no fracture happens, m the Weibull modulus, also called the shape parameter. From a safety point of view, σ_u can be set as zero,[34–36] and thus Eq. 2 is simplified into a two-parameter form.

$$P = 1 - \exp\left[-\frac{1}{V_0}\int\left(\frac{\sigma}{\sigma_0}\right)^m dV\right] \quad (\sigma \geq 0) \tag{3}$$

For indirect measurements of tensile strength, e.g., crushing, knife-edge cutting, and three-point bending, shown in Figure 4, the stress distributed in the specimen is a function of position, and Eq. 3 can be integrated to

$$P = 1 - \exp\left[-\frac{V_E}{V_0}\left(\frac{\sigma_f}{\sigma_0}\right)^m\right] \tag{4}$$

where

$$V_E = K_V V = \int\left(\frac{\sigma}{\sigma_f}\right)^m dV \tag{5}$$

In Eq. 4, σ_f is the maximum tensile stress in the specimen at failure, often called the fracture stress used as the tensile strength of the specimen. The K_V is a loading factor describing the fraction of the specimen volume which is effectively under maximum stress, and is always smaller than unity.[39] The product of K_V and V, i.e. V_E, is referred to as the effective volume under tension and can be pictured as actual volume of the tested specimen effectively under uniform tension at a stress of σ_f. The value of K_V, which is a function of the Weibull modulus, depends on the loading mode and the specimen geometry.[39] For instance, Neergaard[40] gave the K_V for tablets in diametral compression as

$$K_V = \frac{4}{\pi} \times 0.21209 \times m^{-0.48338} \quad (1 < m < 30) \tag{6}$$

and Margetson and Sherwood[41] deduced the K_V for cylinders in three-point bending as

$$K_V = \frac{1}{2\pi^{1/2}} \frac{\Gamma\left(\frac{m+1}{2}\right)}{(m+1)\Gamma\left(\frac{m+4}{2}\right)} \tag{7}$$

in which Γ is the gamma function.

If all of the tested specimens have the same volume, then the volume effect, V_E/V_0 term, is a constant, which is usually merged into σ_0 and disappears in Eq. 4.

$$P = 1 - \exp\left[-\left(\frac{\sigma_f}{\sigma_0}\right)^m\right] \tag{8}$$

where σ_0 is the volume-dependent scale parameter. The scale parameter corresponding to the fracture stress with a failure probability of 63.2% is closely related to the mean strength $\overline{\sigma}_f$ of the distribution.[34,36–38]

$$\overline{\sigma}_f = \sigma_0 \Gamma\left(1 + \frac{1}{m}\right) \tag{9}$$

For the Weibull modulus of 3–20, $\Gamma(1 + 1/m)$ takes values between 0.9 and 1.0, i.e. $\overline{\sigma}_f = (0.9 \sim 1.0) \times \sigma_0$. Note that Eq. 9 only holds for an infinite number of strength measurements. For a limited number of measurements in practice, Peterlik[42] gave an analytical solution for the expectation value of the estimated scale parameter.

Indirect measurement of tensile strength is often practiced for catalyst assessment because of the size and shape limitations of the pellets.[3,4,10,13–16,27–31] For several loading modes, the relationships between the fracture stress σ_f and the applied load F at fracture have been developed according to elastic theory, as follows:

For spheres in diametral compression,[43–46]

$$\sigma_f = \frac{2.8F}{\pi d^2} \tag{10}$$

There exist two points of the maximum tensile stress, symmetrical about the centre of the sphere, on the axis passing through the two loading points, and their locations vary along the loading axis with the strain of the sphere at fracture.

For tablets in diametral compression,[21,47]

$$\sigma_f = \frac{2F}{\pi dl} \tag{11}$$

The maximum tensile stress exists in the plane passing through both the upper and lower contacting lines when measuring the crushing strength. Es-Saheb[48] proposed that Eq. 11 could be applied not only to plane-faced tablets but also to double convex-faced tablets.

For cylindrical pellets in three-point bending,[41,49]

$$\sigma_f = \frac{8FL}{\pi d^3} \tag{12}$$

The maximum tensile stress lies at the opposite point of the central load. In Eqs. 10–12, d and l are the diameter and length or height of the specimens, respectively, and L is the span of bending fixture, i.e. the distance between the lower supports.

For cutting and other measurements, analysis of the fracture stress is possible with a numerical technique such as finite element analysis, and this requires considerable effort. However, similarly to Eqs. 10–12, it is reasonable to assume that the fracture stress is proportional to the load applied to the specimens with identical geometric size,[15] i.e.

$$\sigma_f = \varphi F \tag{13}$$

where φ is a factor dependent on the size and shape of the specimens and the loading mode.

Substituting Eqs. 10–13 into Eq. 8, one obtains

$$P = 1 - \exp\left[-\left(\frac{F}{F_0}\right)^m\right] \tag{14}$$

where $F_0 = \sigma_0/\varphi$. Similarly to Eq. 9, the scale parameter F_0 is related to the mean strength $\overline{F}$ of the distribution.

$$\overline{F} = F_0\,\Gamma\left(1+\frac{1}{m}\right) \tag{15}$$

Equation 8 or 14 is the two-parameter Weibull distribution, applicable to routine test and mechanical reliability analysis of catalyst pellets.

It is worth noting that Weibull statistics was developed based on several basic assumptions.[38,39,50,51] It is supposed that a brittle material fails if any one flaw initiates fracture (the weakest link hypothesis), and that there is no interaction between flaws randomly distributed in sufficient number within the material. For a unimodal Weibull distribution, e.g., Eq. 8 or 14, it is also necessary to assume that there is a single population of flaws that control strength in all the specimens. So, the Weibull distribution may theoretically fail, if any of these assumptions are not satisfied. For example, in the case of the presence of two distinct flaw populations that control strength, the fracture strength distribution will have a bimodal form,[39,52,53] i.e. two straight lines with different slopes, occurring in the Weibull plot like Figure 5A.

Another issue which should be mentioned in the use of Weibull statistics is the size effect on strength, which can be derived from Eq. 4 as

$$V_1\sigma_{f,1}^m = V_2\sigma_{f,2}^m \tag{16}$$

if the flaw population (the Weibull modulus) is independent of the specimen size for the same material.[54,55] The physical interpretation of Eq. 16 is that the probability of failure of a specimen of volume V_2 is equal to that of another specimen of volume V_1, if the stresses $\sigma_{f,1}$ and $\sigma_{f,2}$, applied to the specimens of volume V_1 and V_2, respectively, are related according to Eq. 16. It can also be concluded that the mean tensile strength of a sample is proportional to the $-(1/m)$ power of its specimen volume V.[55,56] Therefore, for brittle materials, the mean tensile strength of a set of large specimens is always smaller than that of a set of small specimens. It can be further explained by the fact that it is more likely to find a large and critical flaw in a large than in a small specimen.[54–56] The Weibull size effect is a useful result as the mechanical properties of specimens at a certain size can be estimated from the observed mechanical properties of specimens at another size. The size effect of strength is the most prominent and relevant consequence of the statistical behavior of the strength of brittle materials. However, the Weibull size effect is not always valid, as discussed in detail by Danzer.[54] So, care must be taken before applying it to the scaling of strength.

Estimation of the Weibull Parameters

There are several methods available in the literature,[34,36,37,56–67] for the determination of the Weibull distribution parameters from a set of experimentally measured strength data. The most widely used method is the linear regression (LR) analysis because of its simplicity. The measured strength data are ranked in ascending order and then a probability of failure P_i is assigned to each strength F_i. Since the true value of P_i is unknown, a prescribed estimator has to be used. The following four expressions are often applied to define the probability estimator.[36,37,56,62–66]

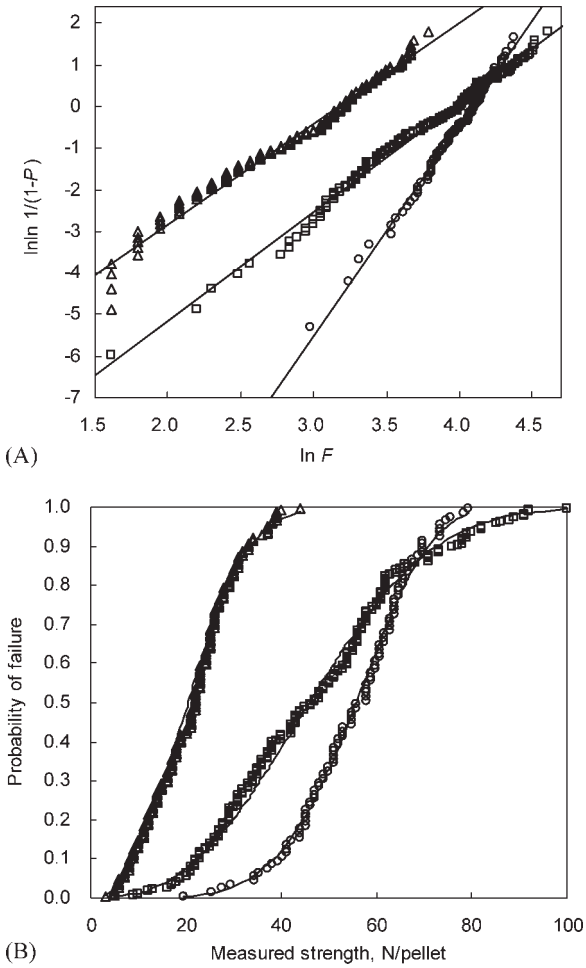

Figure 5. Weibull plots (A) and Weibull distribution curves (B) of the measured strength data of three catalyst samples. (○) a spherical catalyst in crushing; (△) a trilobite catalyst in bending; (□) an extruded cylindrical catalyst in cutting.

$$P_i = \frac{i - 0.5}{n} \tag{17a}$$

$$P_i = \frac{i}{n+1} \tag{17b}$$

$$P_i = \frac{i - 0.3}{n+0.4} \tag{17c}$$

$$P_i = \frac{i - 3/8}{n+1/4} \tag{17d}$$

where P_i is the probability of failure for the ith ranked strength datum, and n is the sample size, i.e., the number of specimens tested.

By taking the logarithm twice, Eq. 14 can be rewritten in a linear form

$$\ln \ln\left(\frac{1}{1-P}\right) = m \ln F - m \ln F_0 \tag{18}$$

So, a linear least-square regression analysis can be performed on this equation. The Weibull modulus is obtained directly from the slope term and the scale parameter is deduced from the intercept term. Figure 5 illustrates the Weibull probability plots and the correlations of three sets of the strength data.

Another method often used for estimating the Weibull parameters is the maximum likelihood (ML) method, according to which the estimators of the Weibull parameters should satisfy the following equations[36,37,61]:

$$\frac{n}{m} + \sum_{i=1}^{n} \ln F_i - n \cdot \frac{\sum_{i=1}^{n} F_i^m \ln F_i}{\sum_{i=1}^{n} F_i^m} = 0 \tag{19}$$

$$F_0 = \left(\frac{1}{n} \cdot \sum_{i=1}^{n} F_i^m\right)^{1/m} \tag{20}$$

Equation 19 may be solved for m with standard iterative procedures, e.g. the Newton-Rhapson method. The scale parameter F_0 is then calculated according to Eq. 20.

Clearly, the ML method needs much more computational effort than the LR method does; however, it has a lower variation coefficient of the estimated Weibull parameters and was therefore recommended as the best estimation method by previous authors.[36,42,62,68]

Mechanical Reliability of Catalyst Pellets

In the reactors, the catalyst pellets may experience various damaging stresses. In most applications, if a small fraction of the catalyst pellets fracture, serious process problems would take place.[3–6] Thus it can be seen that the mechanical performance of the catalyst bed is mainly controlled by those pellets with low strength, rather than all the pellets in the bed. This fact reveals that the low-strength/probability part of the catalyst strength distribution is the key domain for the mechanical reliability, while the mean strength is of less importance by itself.

For any industrial application of solid catalysts, there exists a critical probability of failure of the catalyst pellets, say 5 or 10%, below which the catalyst bed can be normally operated. Weibull statistics provides a method for predicting the fracture load with a specific probability of failure; therefore, the fracture load corresponding to the critical probability of failure can be determined and used to define the mechanical reliability of the catalyst pellets and to compare the mechanical properties between different catalyst samples. The larger the predicted load, the higher the mechanical reliability, and hence the better the industrial performance of the catalyst. As an example, Table 1 gives the data of several commercial high-temperature water-gas shift catalysts.[14] It can be seen that the mechanical reliability of sample 2 is far lower than that of sample 3, though it has the largest mean strength among the six samples.

Equation 14 is Weibull's two-parameter distribution, where m and F_0 are the Weibull modulus and the scale parameter, respectively. For the prediction of the fracture load with a lower level of failure probability, the Weibull modulus has more effect than the scale parameter does.[36,37,65,66] This can be visualized by plotting the Weibull curve according to Eq. 14. While the scale parameter, related to the mean strength with Eq. 15, moves the curve left and right, the Weibull modulus rotates the curve. A higher Weibull modulus leads to a steeper distribution function, a lower dispersion of the mechanical strength, and thus a larger fracture load with the specific lower level of failure probability. Therefore, the Weibull modulus can be regarded as an approximate measure of the mechanical reliability of the catalyst pellets, especially for the case that the mean strength of the compared catalyst samples does not differ much. For catalyst pellets, low strength is related to increased risk of strength failure, and high strength would as a rule result in high pellet density, low porosity, and low catalyst efficiency because of the fact that most of heterogeneous reactions are internal diffusion controlled. Mechanical strength distributed in a narrow window is therefore required for industrial applications of solid catalysts.

It should be explained that the Weibull modulus is an empirical material constant, and depends on the properties of the flaw size distribution in the material. Note that the flaw size should be regarded as an effective or equivalent size rather than an absolute dimension. Some articles tried to predict the mechanical properties and their statistical distributions from the measurement of the flaw properties such as the pore size, combined with computer simulations.[68–70] For brittle materials with the flaw population distributed according to an inverse power law, Jayatilaka and Trustrum[71] gave a correlation between the Weibull modulus and flaw size distribution[50,51]

$$m = 2r - 2 \tag{21}$$

where r is a parameter determining the shape of the flaw size distribution curve. It can be seen that the Weibull modulus is theoretically thought to be only a function of the properties of the flaw size distribution. However, in practice, the estimated Weibull modulus is influenced by the strength measurement, sample size, and estimation method as well as many other factors. A precise estimation of the Weibull modulus is helpful in understanding and optimization of a catalyst material.

Mechanical Properties of Catalyst Packed Beds

Catalysts are often used in packed beds in industry; therefore, the bulk behavior of the mechanical strength is of interest.[10] To study the resistance of a bed of catalyst pellets under compressive loading, the bulk crushing strength (BCS) tests are carried out. In a BCS test, a bed of catalyst pellets is quasi-statically compressed in a cylindrical cup to a specified pressure. After unloading, the material is carefully removed from the cup and a gravimetric analysis is carried out to determine the amount of fines and broken particles. Literature often presents BCS data as plots of percentage of

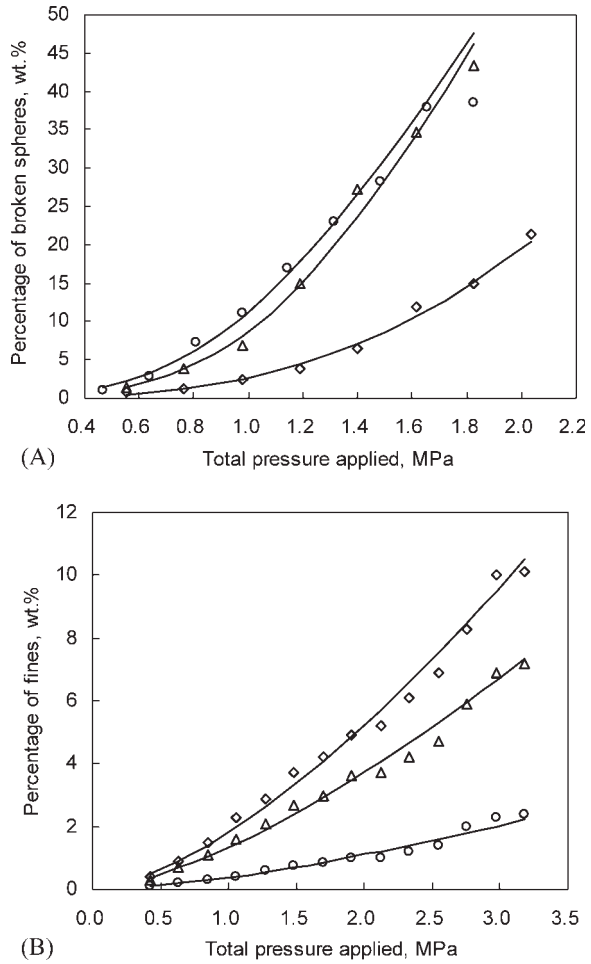

Figure 6. Correlation of the percentage of broken spheres or fines generated with the total pressure applied.

(A) Three spherical samples; (B) one extruded cylindrical sample and fines below the sieves of 1.25 mm (◇), 0.9 mm (△) and 0.45 mm (○), respectively.

fines or broken particles versus the pressure applied on the top of the bed.[1,3,4] The BCS is also defined as the pressure at which 0.5 or 1.0 wt % of fines or broken particles is produced.[72,73]

The BCS have been recommended to be more reliable than the single pellet crushing strength, because it has a closer relevance to packed beds and is presumably applicable to catalysts of all shapes.[1,10,25,26] In 2004, the BCS test was accepted for the first time as a standard method by ASTM.[72] However, a major difficulty encountered in the modeling and correlation of the BCS data to single pellet properties exists mainly because of the uncertainty of the packing and contact behaviors of differently shaped pellets in a packed bed. A number of articles studied the packing density and coordination number by computer simulations,[74–82] while some others presented idealized mechanical models of heaped granular materials.[83,84] Kanda et al.[85] investigated the energy consumption of compressive crushing of small particles by large particles. Ouwerkerk[73] and Couroyer et al.[86–88] simulated the BCS of spherical pellets by a distinct element method.

The dependence of the BCS on the property of single pellets, and the relationship between pellet failure and the pressure drop across the catalyst bed are of primary importance for the design of catalyst, reactor, and process. On the basis of a simplified tetrahedral packing of spheres and force transmission laws, and a reasonable hypothesis that the breaking of a sphere under multi-point pressing also obeys the tensile fracture laws, Li et al.[89] proposed a model for the BCS of spherical catalysts.

$$dw/w = 1 - \exp(-B \times P^M) \tag{22}$$

where dw/w is the mass ratio of broken spheres, P the pressure applied on the top of the bed, B a constant related to the Weibull parameters of the single pellet strength, size of spheres and packing void, and M here is another constant and is predicted to be identical in value to the Weibull modulus of the single pellet strength.[89] For other catalyst shapes, the measure of percentage of broken particles is impractical, but percentage of fines passing a definitive sieve is a more practical index. It has been found that Eq. 22 could be used in this case provided dw/w were replaced by the percentage of fines generated,[90] as shown in Figure 6 for the goodness of fit between the BCS data of several catalyst samples and Eq. 22.

The mechanical failure of solid catalysts results in the formation of fragments and fines, which increases the pressure drop across the reactor. Experimental results show that along with the mechanical failure of the pellets in a catalyst bed, there exists a point of maximum curvature, after which the pressure drop begins to increase rapidly, as illustrated in Figure 7.[6] The rapid increase in the pressure drop does not result from the rapid increase in the amount of broken particles or fines, but from a mutation of the packing structure, occurring as the amount of failed pellets reaches a certain critical value. It is observed that a trilobite extrudate is much easier to result in the pressure drop increase than a cylindri-

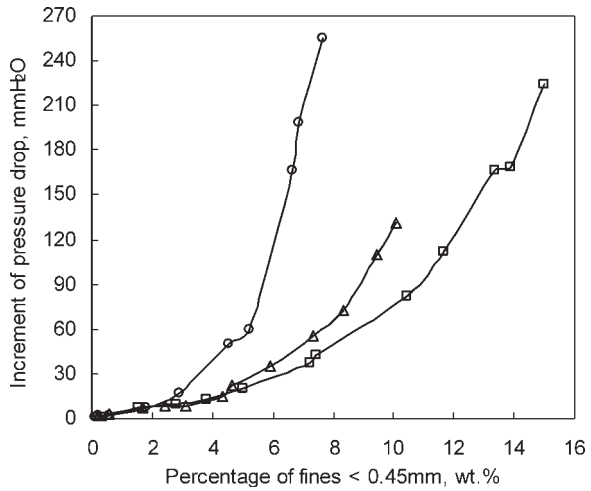

Figure 7. Effect of the percentage of fine particles on the increment of the pressure drop at an air flow rate of 3 m^3/h. (○) a spherical sample; (△) an extruded cylindrical sample; (□) an extruded trilobite sample.

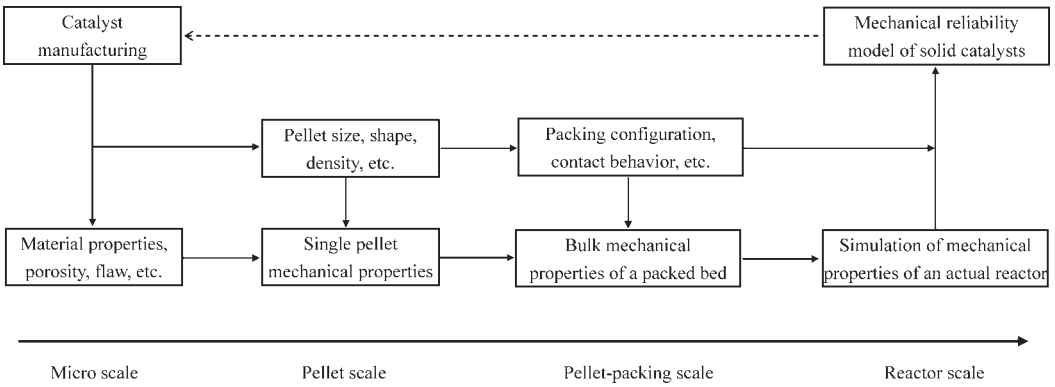

Figure 8. A multi-scale framework for the mechanics of solid catalysts.

cal extrudate, and that a catalyst with smaller pellet size is more susceptible to an increase in pressure drop.[6] One of the possible explanations is that much more debris and fines are generated in the same loading range for the sample with smaller size or trilobite shape. It is also shown that the measurement of pressure drop through a laboratory-scale packed catalyst bed has a satisfactory reproducibility and provides useful information relevant to the mechanical reliability of a packed-bed reactor.

The understanding of the effect of the mechanical failure on the pressure drop is of guiding significance to the estimation of power consumption and the selection of compressor types in engineering design. The pressure drop across a packed bed filled with fresh catalysts with regular shapes can be predicted approximately[91,92]; nevertheless, there does not exist a model up to now which predicts the pressure drop through a catalyst bed in which there are fragments and fines generated from the mechanical failure of pellets.

Perspectives

From manufacturing to industrial application, the catalysts experience a lot of processes, e.g. pelletization, impregnation, transport, loading, reduction, startup, normal operation, shutdown, discharge, etc. All of these have strong effects on the mechanical strength and reliability of the catalysts. For instance, the manufacturing process determines the catalytic material properties, microscopic structure, pellet size and shape, and thus affects the mechanical properties. In other processes, the catalyst pellets are subjected to the reconstruction of structure and subjected to internal or external stresses. Especially, the catalytic reaction is a quite complicated process for the catalyst strength. The mechanical reliability of the catalysts is directly related to the reactor configuration, catalyst-loading mode and height, reaction condition, and reactant properties. These facts tell us that an integrated research on catalyst mechanical properties should involve all the processes mentioned earlier, rather than only catalyst pellets itself. The objective of the research on catalyst mechanics is to establish a mechanical reliability model of solid catalysts under specific operational conditions. It is expected that given the single pellet properties of the catalysts, the mechanical reliability of a reactor could be predicted and then the permissive catalyst-loading mode and operational conditions could be determined. On the contrary, it is also expected that given the catalyst-loading mode and operational conditions, the single pellet properties of the catalysts could be ascertained and then the catalyst manufacturing could be instructed. Figure 8 shows a typical multi-scale framework for the mechanics research of the fixed bed catalysts.

Effect of the material properties and microstructure on the single pellet mechanical properties

The mechanical properties of solid catalysts are closely related to the material properties and microstructure of catalyst pellets. Griffith equation reveals that fracture strength depends on the elasticity modulus, surface energy, and crack size in the catalyst bulk.[17] Weibull statistics shows that the Weibull modulus only relies on the flaw distribution in the catalyst material.[71] Knudsen[93] considered that the catalyst-crushing strength is a function of the porosity and the diameter of the primary particles from which the catalyst pellets are made up.[94] Rumpf[95] outlined the binding forces inside agglomerated materials such as catalysts. He proposed that the forces like solid bridges, interfacial forces and capillary pressure at freely movable liquid surfaces, adhesion and cohesion forces at not freely movable binder bridges, attraction forces between solid particles, and formed-close bonds or interlocking, are the major reason for holding the macroscopic particle agglomerate structure. Pietsch[96] classified these forces into two groups: binding with material bridges and binding without material bridges. In agglomerated materials, there are well-developed crystal edges and pores, which are randomized flaws. Johnson et al.[97] have developed the original work by Rumpf. They considered the work of adhesion and concluded that there is an inverse relationship between the tensile strength of agglomerates and the primary particle diameter.

It is known that the manufacturing process determines the catalytic material properties and microstructure, and hence the mechanical properties. Catalyst developers like to study the process factors to optimize the manufacturing process and to improve the mechanical properties of solid catalysts,[98–103] while the theoretical issues in the manufacturing process are rarely involved. So, the quantitative correlation between the material properties, microstructure, and the single pellet mechanical properties is still lacking although

the qualitative analysis can be found occasionally in the literature.

Correlation between the single pellet and bulk mechanical properties

There are many similar aspects between a practical fixed bed reactor and the small packed bed used in BCS test. For instance, random packing of the catalyst pellets might have the same nature between large and small beds. The major force in the practical reactor is normally also axial, which is composed of the weight of the pellets themselves and the pressure drop of the fluid phase. In general, the BCS measurement may be regarded as a most simplified model for the operation of the practical reactor.

If the translation from the single pellet strength to the BCS can be made, it can be expected that the bulk behavior of the catalyst packing can be predicted in the term of the single pellet properties of the catalyst. In the other way around, for a specific reaction system, the single pellet specifications can be defined precisely. For instance, the pellet formation conditions could be optimized for the final use of the catalyst, and hence the pellet density of the catalyst could be optimized. The correlation between the single pellet and bulk mechanical properties provides a possibility for the reliability prediction of a reactor. These benefits may lead to a great economical advance of the processes.

Simulation of the mechanical reliability of the actual reactor

It is evident that there exist differences between a practical fixed bed reactor and the small bed used in BCS test. For example, in the reactor, catalysts usually are heated and expanded, and thus a repulsion force will appear between pellets in the radial direction, which increases the effect of the external stress on the catalyst strength. Moreover, solid catalysts are multi-crystal powder agglomerates. Different orientations between crystal grains within the catalyst material and different heat-expanding coefficients between phases lead to different expending degrees in different directions, and then causes stress concentration at phase interfaces; that is, a thermal stress is induced inside the pellets, which changes the mechanical properties of the catalysts. Reactants have also effects on the catalyst strength. The fluid will impact and erode the catalyst pellets. The adsorption of the reactants on the internal surfaces of the catalysts reduces the surface energy of the materials, and thus reduces the fracture strength of the catalysts. In conclusion, the operational conditions of the reactor have significant influences on the mechanical strength and reliability of the catalysts.

The simulation of the mechanical properties of the catalysts for real reaction conditions, e.g. specific temperature, pressure, flow velocity, and existence of liquid film, is needed to establish the mechanical reliability model of solid catalysts. Moreover, the evolution of the mechanical properties of the catalysts with varying conditions is of guiding importance to efforts at increasing their mechanical reliability. Even more important, the evolution of the mechanical properties with time, i.e. catalyst fatigue strength, should also be addressed. Fortunately, the BCS device has been established and the BCS model has been put forward. And there is a great possibility of doing experiment in reaction conditions with the configuration of present BCS apparatus, and there is strong reasoning for the applicability of the BCS model or its adjustment formula to the data of the reaction conditions experiments.

Concluding Remarks

Mechanical strength of solid catalysts is one of the most important factors for the reliable and efficient performance of a reactor. Some recent developments on the basic mechanics of solid catalysts are reviewed in this work. The main concepts discussed are the brittle fracture which leads to the mechanical failure of the catalyst pellets, the measurement, and statistical properties of the catalyst strength data, the mechanical reliability of the catalyst pellets, the mechanical properties of the catalyst packed beds, etc. Furthermore, it is pointed out that an integrated research on catalyst mechanical properties should involve all the processes from catalyst manufacturing to industrial application, rather than only catalyst pellets itself. For this purpose, a multi-scale framework for the mechanics of the fixed bed catalysts is proposed. It is expected that a mechanical reliability model of solid catalysts could be established under specific operational conditions.

Now many topics of research on catalysis are passing from craft to science. However, because of the complexity of the mechanical properties of solid catalysts and their reactors, the understanding on this subject is still very poor. The scientific basis for the issues on the catalyst mechanical properties calls yet for further elucidation and advancement.

Acknowledgments

Financial supports from the Natural Science Foundation of Jiangsu Province of China (Project Number: BK2007119), the Science and Technology Foundation of Southeast University (Project Number: XJ0619243), the Teaching and Research Program of Southeast University for Excellent Young Teachers, the NSF of China (Project Number: 20076034, 20576097), Ministry of Education and SINOPEC Tech. are gratefully acknowledged.

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Manuscript received May 29, 2007, and revision received July 19, 2007.