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Understandings on the scattering property of the mechanical strength data of solid catalysts

A statistical analysis of iron-based high-temperature water-gas shift catalysts

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Abstract

Statistics reveal that horizontal crushing strength data scatter in rather large ranges for cylindrical iron-based high-temperature water-gas shift catalyst tablets. This scattering is due to brittle fracture nature of the strength failure, originating from the stress concentration around edges of existing micro-cracks, such as pores, defects, and discontinuations contained in tablets. However, variations in the tablet size and density are found to contribute to strength data scattering. Data of tablet strength, height and density of the catalysts are found to be scattered in different ranges and to follow Weibull distribution, respectively. Based on the statistical data from a number of commercial catalysts, strength failure probability is proposed as the critical parameter for quality control. Catalyst tablet texture is examined, and it is observed that the tablets with strength close to low end of strength distribution have higher porosity, lower density and larger pore size in comparison with those near high end. For catalyst tablets, low strength is related to increased risk of strength failure, and high strength would result in lower catalyst efficiency. Catalyst tablet strength distributed in a narrow window is beneficial for commercial application. A correlation between catalyst tablet density and strength is established using a model proposed by Knudsen. Results obtained by analysing these interrelated parameters indicate that optimisation of catalyst tablet mechanical strength can be achieved through monitoring and controlling material properties and processing parameters during preparation.

Keywords: Mechanical strength; Iron-based water-gas shift catalyst; Statistical analysis; Weibull distribution; Texture properties

1. Introduction

Mechanical strength of catalyst pellets is an important factor to ensure reliable performance for fixed bed reactors [1,2]. An AIChE committee has convened in 1974, and extensive discussions on mechanical strength and other application issues have been made in order to set up a US standard [3–9]. Several methods, such as crushing strength of a single tablet, have since been accepted as standards in many countries [10–12]. However, there has been a lack of literature on the explanation of the scientific basis

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for these measurements. Catalysis research has emphasised on improving of strength by different methods, as indicated in [13–18]. Some authors have tried to define the nature of the catalyst mechanical strength [19,20] and establish correlation with other physical properties [21–23]. However, studies on the mechanics of other type porous materials such as soils and ceramics have been a very active field and have given much insight [24–36].

Based on the examination results of several working catalysts, Hutchings [37] proposed that the crushing strength of catalyst pellets can be used as a diagnostic test for catalyst mechanical strength. Nevertheless, the statistical nature of the crushing strength of solid catalysts has been ignored unreasonably, as evidenced by the very recent American standard [12] and the catalyst brochures of some important suppliers [38,39], which require or give crushing strength data only as mean or approximate values. It has been found that strength failures of mixed oxide catalysts under laboratory testing and industrial application conditions are both cases of brittle fracture [40]. The expending of the micro-cracks existing in the tablets under the tensile stress concentrated at their edges is the primary reason for fracture [41]. Thus the measured values of the strength should have a direct relationship to the maximum tensile stress leading to fracture. For cylindrical tablets, the method proposed by Wright [42] for the measurement of tensile strength of concrete materials, i.e. the horizontal crushing strength (HCS) of cylinders, can be used which is based on a relationship between the tensile stress and loading existed based on the elastic theory of material. It has been well established that the tensile strength data of brittle materials do not follow normal distribution, but follow a Weibull distribution [43]. Furthermore, due to the large scattering range of the strength data of brittle materials, as evidenced by that in Hutchings [37], the mean values are not informative enough. Weibull distribution has been successfully used in the description of the probability of strength failure of brittle materials for a long time. In previous publications from this group, this probabilistic method has been used in the description of the strength properties of solid catalysts [40,44–47].

It has been found that the HCS data of cylindrical tablets of iron-based high-temperature water-gas shift (HTWGS) catalysts follow the Weibull distribution [40], and this provides a method for calculating the probability of catalyst strength failure under a specific stress condition. The brittle fracture nature of the strength failure, coupled with the elastic behaviour of the catalyst materials, under low load during strength measurement has enabled us to correlate processing parameters in catalyst preparation and handling with the strength [44–47]. Several operational schemes have been demonstrated to be successful at optimising parameters in tabletisation, calcination and reduction [44, 46,47]. Very reliable samples, e.g. one in oxidised state with a probability of failure under 10 kg/tablet as low as 6.65×10^{-13} and another in reduced state with this probability as low as 4.16×10^{-11}, has been reported [46,47].

While examining commercial HTWGS catalysts, some relationship between the mechanical properties and their textures has been found. This paper discusses the statistical features of mechanical properties of these catalysts, which have not been described in literature.

2. Experimental

2.1. Catalyst samples

2.1.1. Commercial tablet samples

Tablet samples used in this study are among the most popular commercial iron–chromium-based HTWGS catalysts now available in Chinese market. Table 1 gives a general description of catalyst physical properties in oxidised state. In the table, samples 1–4 are in plane-faced cylindrical form, and their densities and sizes are measured rather precisely. Samples 5–6 are double convex-faced cylindrical tablets, while their diameters can be measured, their heights given in the table are the nominal values of the total height taken from the product brochure of the supplier. As the size of the convex part is rather difficult to determine, their densities are omitted.

2.1.2. Powder samples

Two powders were used in the analysis of the relationship between the density and strength. One (referred to as p1) was taken directly from the production line of tablet sample 2, but was the material after calcination and before tabletisation. The other (referred to as p2) was a powder material also taken from a

Table 1
Description of the commercial tablet catalyst samples used in this work

No	Nominal size (mm)		HCS measured in lab					Mean density (g/cm^3)
	Diameter	Height	Mean value (kg/tablet)	Standard deviation	Number of tablets measured	Minimum value	Maximum value	
1	9.1	5.17	27.5	8.64	69	9.50	48.3	1.72
2	9.1	6.59	34.2	11.2	75	12.9	66.9	2.32
3	9.6	4.79	30.0	5.25	73	18.0	40.2	1.95
4	9.6	4.91	23.3	4.38	72	14.9	36.0	2.00
5	5.4	3.6	17.3	6.48	58	3.40	30.0	N/A
6	6.0	6.0	17.1	5.17	39	8.80	29.7	N/A

commercial production line, after calcination and before tabletisation. p1 contains around 10 wt% of Cr_2O_3 and 90 wt% of Fe_2O_3. p2 has around 8 wt% of MoS_2, with Cr_2O_3 and Fe_2O_3 in the same ratio as in p1. The powder materials were tabletised directly at various pressures in a range 1–5 kbar/cm^2 in the laboratory with an equipment described elsewhere [44], and with the addition and uniform mixing of 1 wt% graphite, and crushing and sieving to pass a sieve of 20 mesh. One another sample (referred to as pf) was used which was a spent catalyst after industrial service, and which was replaced due to strength failure. It looked like a mixture of particles and powder. Its history and composition are not known due to its commercial origin.

2.2. Physical properties measurement

The scale used to measure the size of the tablets was graduated to 0.01. The balance used for the measurement of the weight was accurate to 0.0001. The HCS data were measured by a MQ-200 strength tester made in Dalian, China. The tablets were pressed in a radial direction, with insertion of two pieces of filtration paper in between the tablet and the lower and upper anvils of the tester, which ensures a uniform distribution of the load along the contact lines. Before measurement, the catalyst samples were heated in air at 250°C for 24 h. The texture data were collected by an Autopore 9220 II porosimeter.

2.3. Data treating

2.3.1. Weibull statistics for strength

A two-parameter Weibull distribution equation is given by Weibull [43]

$$F(\sigma) = 1 - \exp(-\beta_0 \sigma^m), \tag{1}$$

where $F(\sigma)$ is the probability of strength failure, σ the maximum tensile stress leading to fracture, β_0 the size parameter of the Weibull distribution, and m is the Weibull modulus. An analytical solution of the equations of elastic mechanics, for tensile stress developed in an ideal disc, with opposing two point loading is available. The following approximate relation is often used to correlate the maximum tensile stress and loading for a plane-faced disc like specimen with limited height [48,49]:

$$\sigma \approx 2P/\pi dl. \tag{2}$$

This stress exists in a plane passing through both the upper and lower contacting lines when measuring the HCS. In Eq. (2) P is the total load in HCS measurement, d the diameter and l the height. For the double convex-faced cylinders, Es-Saheb [36] recently illustrated that Eq. (2) can be used approximately with the introduction of a constant. Anyway, it is reasonable to assume that the maximum tensile stress leading to fracture is proportional to the total loading in the HCS measurement for all cylindrical tablets listed in Table 1. Combining (1) and (2), we get

$$F(P) = 1 - \exp(-\beta P^m), \tag{3}$$

which can be put into the form

$$\ln\ln\left(\frac{1}{1 - F(P)}\right) = m \ln P + \ln \beta. \tag{4}$$

The maximum loading P can be measured, and $F(p)$ can be estimated by listing the HCS data from the minimum to the maximum value, i.e.

$$P_1, P_2, \cdots P_i \cdots P_{n-1}, P_n$$

The probability can be estimated by

$$F_i(P) = \frac{i}{n+1}, \tag{5}$$

in which i is the ith sequential number of the data, n the total number. This estimator is considered conservative by several investigators [50–52], which gives a slight under-estimation for the Weibull modulus, and a slight over-estimation for the probability of failure. The Weibull parameters can be obtained by linear least square regression between the P_i and $F_i(P)$.

2.3.2. Statistics of height and density

A Weibull distribution was used to describe the height and density distributions of commercial catalyst tablets. The Weibull parameters for height, denoted as m_l and β_l, and density, denoted as m_d and β_d, were obtained with the same regression method as described above.

2.3.3. Correlation between density and strength

Density has a major effect on mechanical strength of porous materials. Many authors proposed models to correlate strength and density [21,22,53]. After a preliminary test of models existing in literature, it was found that a model proposed by Knudsen [53] can be used to fit data quite well. This Knudsen equation is given as

$$\sigma = \sigma_0 \exp(-b\mu), \tag{6}$$

in which σ_0 is the theoretical strength when there are no pores, μ the porosity of the material, and b is a constant. For a material, its porosity and density relationship is defined as

$$\mu = 1 - \frac{\rho}{\rho^0}, \tag{7}$$

where ρ is the real density, and ρ_0 the theoretical density. For a brittle material, it has been found that the strength is dependent on the size of the test specimen [54]

$$\sigma = cl^{\alpha}, \tag{8}$$

in which c and α are the constants for a specific material, and α is normally smaller than unity for any brittle material. Combining Eqs. (2), (6), (7) and (8)

$$P = Al^{\delta} \exp(\lambda\rho), \tag{9}$$

in which A, δ and λ are the constants. δ was found to be very close to unity for these iron-based catalysts. In this paper, $P/l \sim \rho$ is plotted to verify the effect of density.

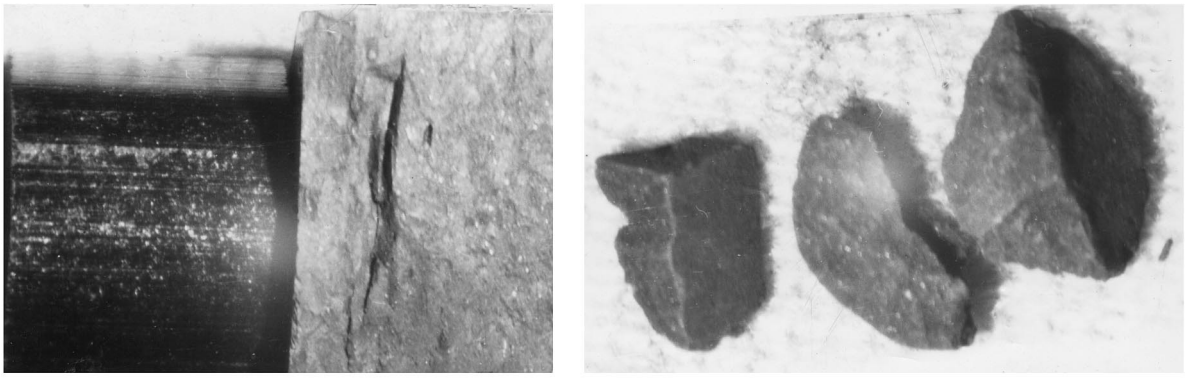
3. Results

3.1. Tablets fracture

It was observed that, when measuring the data of HCS, brittle fracture happens along the plane passing across the upper and lower contacting lines, which most frequently results in two half tablets. However, fracturing to many pieces was also observed, which happens most probably when the strength of a specific tablet is very high. The fracture surface was not smooth but rather irregular, and has the features of brittle fracture, indicating the growth of the micro-cracks leading to the fracture. The selected particles from failed commercial catalyst p_f also show that their surfaces were formed due to brittle fracture. Fig. 1 gives the photographs of a cylindrical tablet after the measurement of HCS, and that of the particles selected from the failed sample.

3.2. Statistics of the strength of the commercial catalyst tablets

The brittle fracture nature of the strength failure leads to a large scattering range of the data. As shown in Table 1, the differences between the maximum and the minimum values of HCS data are often larger than the mean values of the corresponding catalyst tablets, which makes the mean value of data uninformative. A useful distribution function is needed to describe the HCS data and to calculate the probability of failure of a catalyst. Very fortunately, a Weibull distribution [43] is applicable for these purposes. Fig. 2 depicts the quality of fit of the HCS data with Eq. (3), where solid lines are curves predicted by the equation and the points are measured values. It can be seen that these data are fit quite well. Table 2 gives the Weibull parameters of these samples and their probability of strength failure under several critical loading conditions.



(a) (b)

Fig. 1. The fracture pieces in different cases. (A) two major pieces of a tablet after measuring its horizontal crushing strength. The smooth part (left) is the outer surface of the tablet, the right part is the fracture surface. (B) pieces selected from a failed commercial catalyst after industrial application.

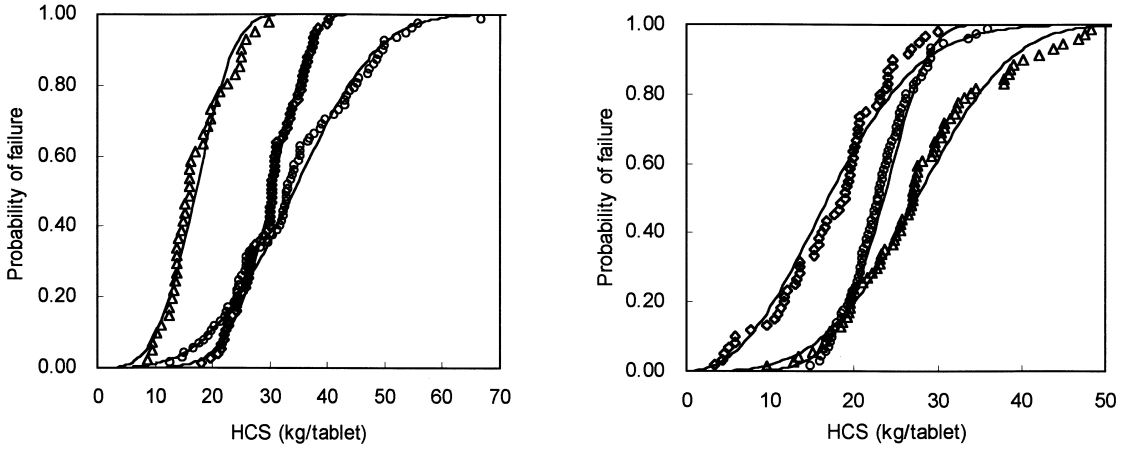


Fig. 2. Weibull distribution curves of HCS data of the catalyst samples in Table 1. Left: (△) sample 6; (◇) sample 4; (○) sample 2. Right: (△) sample 1; (◇): sample 5; (○) sample 3.

Table 2
Weibull parameters and probabilities of failure under critical loading conditions for commercial catalyst tablet samples

No	Weibull modulus	Weibull size parameter	Probability of failure under different loadings (kg/tablet)			
			5	10	15	20
1	3.58	4.76×10^{-6}	1.51×10^{-03}	1.79×10^{-02}	7.44×10^{-02}	1.95×10^{-01}
2	3.41	4.09×10^{-6}	9.89×10^{-04}	1.05×10^{-02}	4.10×10^{-02}	1.06×10^{-01}
3	6.45	1.91×10^{-10}	6.16×10^{-06}	5.38×10^{-04}	7.33×10^{-03}	4.60×10^{-02}
4	6.22	2.03×10^{-9}	4.52×10^{-05}	3.36×10^{-03}	4.11×10^{-02}	2.22×10^{-01}
5	2.31	1.00×10^{-3}	4.03×10^{-02}	1.85×10^{-01}	4.06×10^{-01}	6.37×10^{-01}
6	3.70	1.88×10^{-5}	7.22×10^{-03}	8.99×10^{-02}	3.45×10^{-01}	7.06×10^{-01}

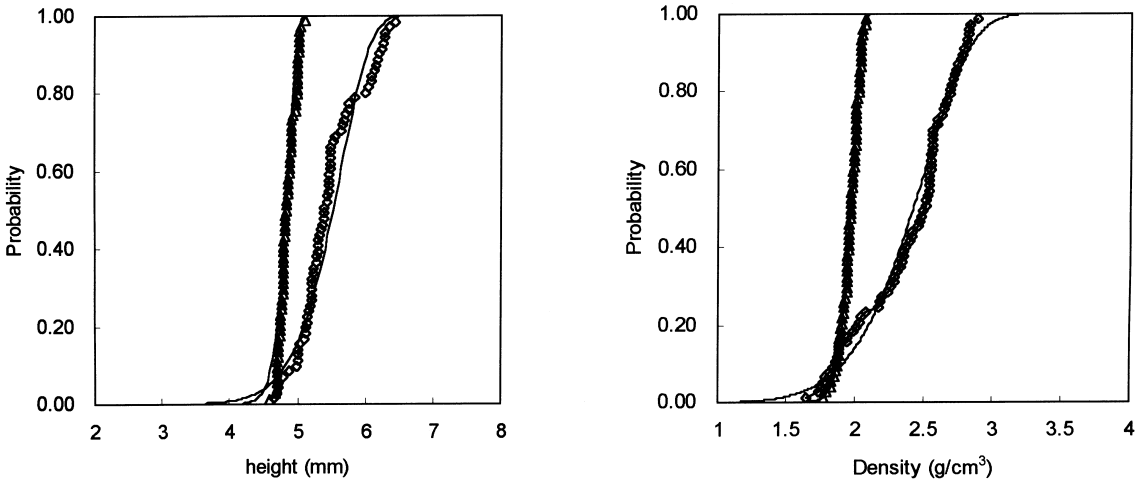


Fig. 3. Height and density distribution of catalyst tablets correlated with Weibull distribution function. Left: height; (◇) sample 1; (△) sample 4. Right: density; (◇) sample 2; (△) sample 4.

3.3. Statistics of the height and density of the tablets

For commercial catalyst samples, tablet size and density are also scattered in different ranges. It was found that the distribution of height and density of the plane-faced tablets are described well by a Weibull distribution. The fit of these data with the function are shown in Fig. 3, in which the points are the measured values and the curves were predicted by the equation after obtaining regression parameters. Table 3 lists the Weibull parameters of the height and density distribution of the four plane-faced samples.

3.4. Tablet texture

From the data presented in Table 1 and in Fig. 2, it can be seen that the HCS data of all these samples scatter in rather large ranges. To understand the properties of tablets at the two extreme ends of the distribution, these major pieces after HCS measurement of the tablets with strength either near the minimum or the maximum end were taken for texture measurement. The major fracture pieces of five tablets were taken for each sample, and were mixed before sending to the instrument laboratory. Due to the fact that one measurement may not need so much material, it is possible that only part of these particles was used and the data were derived from one or two tablets of the five. Table 4 gives the textural data of the tablets with strength near the highest and lowest of the commercial tablet samples, and the corresponding mean HCS of the five tablets. The data show that large differences for all the texture properties exist for all the samples both in the low and high end of strength distribution. The pore size distribution curves of four selected samples are illustrated in Fig. 4, indicating that deviations of the two curves of different samples are rather dissimilar.

Table 3
Height and density distribution parameters for the plane-faced tablets

No	Height		Density	
	m_l	β_l	m_d	β_d
1	14.1	2.26×10^{-11}	12.0	2.57×10^{-4}
2	14.2	1.73×10^{-12}	8.08	5.53×10^{-4}
3	56.4	7.02×10^{-39}	48.2	2.08×10^{-14}
4	52.0	1.28×10^{-36}	36.6	1.18×10^{-11}

3.5. Correlation between density and HCS

As for the tablets formed in industry have comparatively small range of deviation of density and size in the point of correlation of the data, so that the powder materials are used to examine this relationship. Tabletizing of powders from industry in the laboratory was done with a random variation in pressure and filling

Table 4
Texture data of tablets in high and low end of strength distribution

No	Mean HCS of five extreme tablets (kg/tablet)	Skeletal density (g/cm^3)	Tablet density (g/cm^3)	Porosity (ml/g)	Surface area (m^2/g)	Mean pore diameter (um)	Ratio of pore volume in specific diameter range (%)	
							>50 nm	>20 nm
1	45.9	4.55	2.24	0.226	50.8	0.0178	3.50	39.8
	14.2	4.30	1.60	0.391	47.4	0.033	35.6	85.8
2	45.9	4.07	2.11	0.229	58.6	0.0156	11.8	37.3
	19.8	4.08	1.58	0.389	67.4	0.0231	22.4	70.7
3	31.0	4.65	1.95	0.299	39.4	0.0304	8.60	89.5
	38.3	4.54	1.86	0.316	38.3	0.0330	10.0	92.0
4	37.8	4.73	1.85	0.329	42.1	0.0313	14.0	90.2
	21.8	4.73	1.74	0.365	44.1	0.0331	20.0	91.3
5	23.1	4.29	1.94	0.284	43.9	0.0258	5.00	83.0
	8.0	4.24	1.87	0.300	49.9	0.0240	8.00	82.0
6	24.6	4.30	1.94	0.282	43.6	0.0259	6.00	83.0
	9.9	4.27	1.72	0.348	44.6	0.0312	20.1	89.2

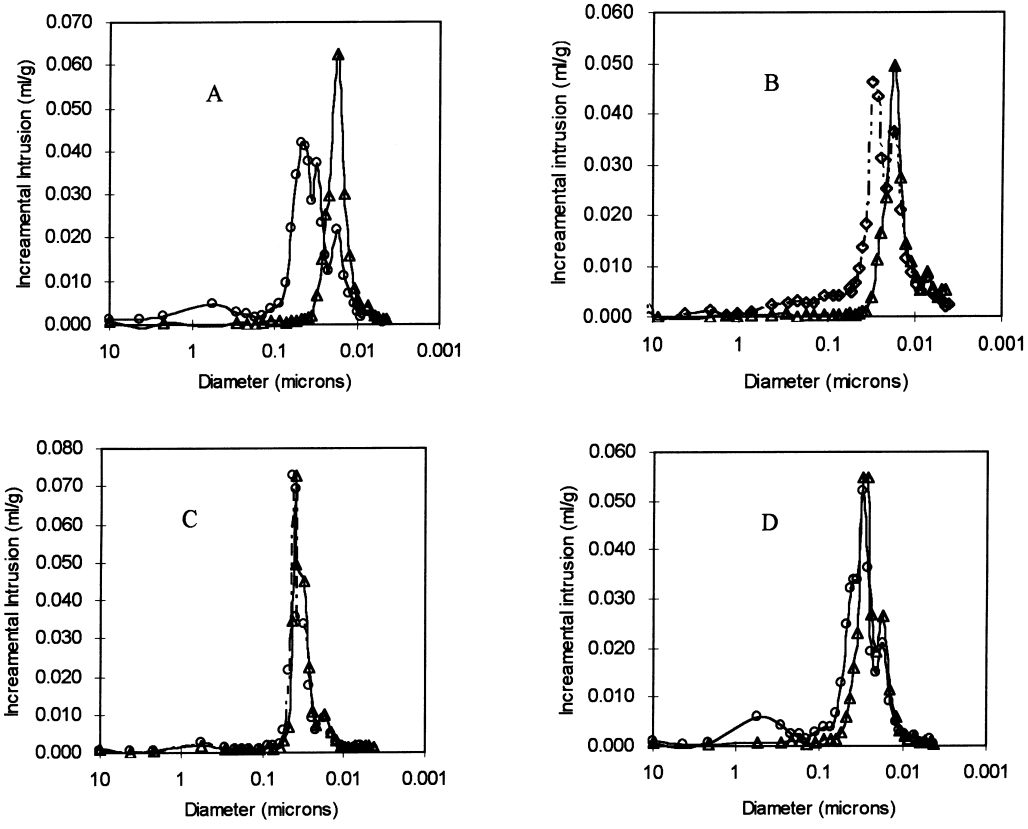


Fig. 4. Pore size distribution of commercial catalyst tablets measured by mercury porosimetry method. (○) Tablets with strength near the lowest end of the distribution; (△) tablets with strength near the highest end of the distribution. (A) sample 1; (B) sample 2; (C) sample 4; (D) sample 6.

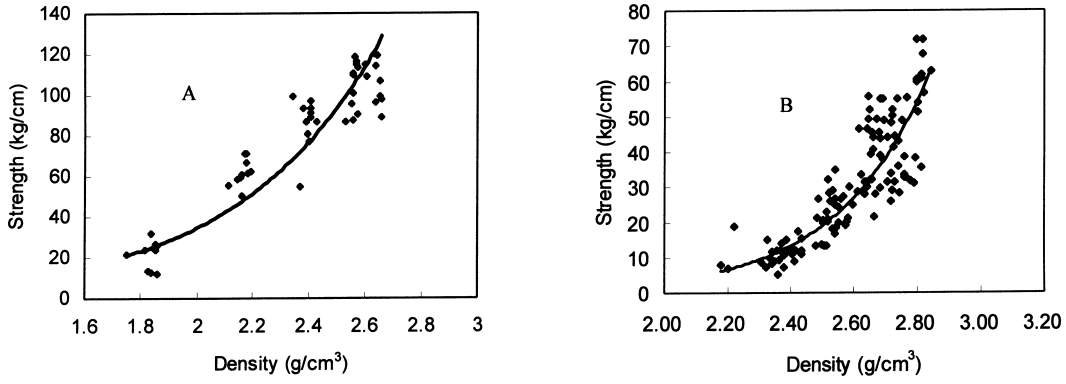


Fig. 5. Relationship between strength and density. (A) p1; (B) p2.

weight, so that a comparatively large range of density and size were obtained. However, these ranges are still strongly limited by the tabletizing process. Furthermore, these factors do not follow normal distribution, and as a consequence, such a correlation has a comparatively large uncertainty from a mathematical point of view. The relationship and the quality of the correlation are presented in Fig. 5. The two constants A and λ, when assuming $\delta=1$, are 0.645 and 1.99 for p1, 0.0029 and 3.52 for p2, respectively.

4. Discussion

4.1. Comparison of the catalysts

The data in Table 1 indicate that all these samples have a common feature, i.e., all have a rather large scattering range of the strength data. We define a factor to characterise the deviation of the data as

$$D_m = (M_a - M_i)/M_m, \tag{10}$$

where M_a is the maximum, M_i the minimum and M_m the mean values of the HCS data, it can be calculated that D_m equals to 1.41, 1.58, 0.740, 0.906, 1.54, and 1.23, respectively, for six samples. This means that four out of the six samples have differences between the maximum and the minimum values larger than their mean values. Such a large deviation in strength data makes the report of the measurement according to the standards [12], i.e. the average strength and the standard deviation of the data, uninformative. As the data in Table 1 shows, sample 2 has the maximum value of mean HCS. However, taking into account the deviation of its data, it cannot be concluded that this sample would have the best mechanical reliability.

The comparison of the mechanical strength between different samples is however, very important both for a user and a manufacturer. An argument often heard from the catalyst users and researchers is that a catalyst should have been tested extensively before it is commercialised, and the mechanical reliability of a catalyst ought to be guaranteed by the supplier. Nevertheless, because the mechanical properties of the catalyst are very sensitive to the production factors, storing and the transportation conditions [45], a routine test of the catalyst purchased is good for the users. The producers need to compare batches and to make repeatable products. If a probabilistic method is introduced, an informative comparison of catalyst strength can be expected.

Fig. 2 shows that the fit of HCS data is fairly good for all samples with a Weibull distribution. This result allows us to calculate the probability of strength failure at a specific load condition for cylindrical tablets. The Weibull parameters obtained by regression and the probabilities of failure at several radial load conditions are given in Table 2. It can be seen that the ranking of the samples by probabilities of failure is completely different than from that by their average values. As for the industrial performance of a catalyst, the probability of failure under a critically low loading is of much more concern than that under high loading. Furthermore, these six samples have been proved to be successful in industrial application and are representative of the status of the iron-based HTWGS catalysts

in aspects of size, form and chemical composition. We suggest that one use the probability of failure at 10 kg/tablet as the critical value for comparison of these catalysts. It can be also seen that the sequence of the Weibull moduli m and the deviation D_m of the data are almost the same as that of the probability at low loading conditions. However, the probability of failure at 10 kg/tablet is more direct for the reliability comparison.

Following is further explanation why we propose that 10 kg/tablet is appropriate for comparison. From the data in Table 2, sample 5 has the maximum probability of failure under this condition, and is 18.5%. All others have this value lower than 10%, but sample 5 has been proved to be adequate in industry. Therefore, it is rather sensible to use the probability of failure at this loading condition as the critical point for comparison of this catalyst. The difference in size between the samples in the comparison may be ignored because of the fact that the different samples have only small differences in size and in the mean value of HCS data.

4.2. Strength distribution

The applicability of a Weibull distribution to these data provides a possibility for the reliability prediction of a working catalyst. Although the mechanical properties of the cooled tablets may be quite different from that under reaction conditions, and there are still difficulties in the correlation between mechanical reliability of single tablets and those in a packed bed, it is a very good starting point for modelling.

A narrow distribution of catalyst strength is beneficial. However, several factors influence the strength distribution. The Weibull equation is based on several hypotheses. Firstly, a weakest linkage model which assumes that in the material the weakest crack leads to the fracture. Secondly, a common distribution of the extreme stress with which all the micro-cracks follow. Thirdly, a uniform distribution of the tensile stress in the space concerned. Ideal materials, which have no cracks and dislocations, have a very high Weibull modulus and hence very narrow distribution of the tensile strength data [55]. For porous catalysts full of defects, dislocations and discontinuations in the body of tablets, these are in the same range of size and nature as the micro-cracks defined by fracture mechanics, which are the origins of stress concentration. Therefore, the scattering of the strength data of catalysts is one of the intrinsic properties of the brittleness of the materials. According to Griffith equation [41],

$$\sigma = (2Er/\pi C)^{1/2}, \tag{11}$$

the strength of a brittle material is dependent on the Young's modulus E, the surface energy of the material γ, and the factor C, which is a statistical number characterising the size, direction and strength distributions of the micro-cracks existing in the materials. According to Knudsen [53], the Young's modulus is a function of the porosity, thus the deviation of the density contributes to the scattering of the HCS data. The Weibull equation has a constant β, which is dependent on the size of the space in which the maximum stress exists [43]. Therefore, the scattering of the height of the catalyst tablets contributes to that of strength data.

Some of the experimental evidence for the size and density distributions taking a role for the strength scattering is shown in the data of Table 3. Catalyst samples 1 and 2 are domestic made products, manufactured using different techniques. For instance, one was made by coprecipitation, and the other was produced by a wet mixing technology. However, the same brand of tabletising machines were used. The samples 3 and 4 are from an overseas supplier. It can be seen that samples 1 and 2 have very similar values of the Weibull modulus of HCS, height and density, and that samples 3 and 4 have these values very close to each other too. In addition, when the powder material of sample 2 was tabletised in laboratory with a specially designed tabletising equipment to ensure the precision of the die and punch, we have obtained the Weibull parameters of the HCS data as, m=10.1 and β=1.22×10^{-17} [47].

4.3. Tablet texture

It has been well established that most of the commercial heterogeneous catalytic processes, such as the HTWGS, are operating under an internal diffusion limited condition [56]. Therefore, the texture properties and especially the pore size distribution are very important for efficient performance of the catalyst. The data in Table 4 shows that high strength tablets

within the same sample have a higher tablet density, a lower porosity, and lower ratios of macropores and mesopores in the higher diameter range [57]. Although the surface area in the measured range has two irregular results, i.e. sample 1 and sample 3, the others are in the same sequence.

The smaller the pore size, and the lower the porosity, the more severe the diffusion limitation is. Therefore, tablets in the range near the highest end of the strength distribution are lower porosity and contribute little to the total processing ability of the converter, while tablets in the range near the lowest end of the distribution are at more risk of strength failure. As a consequence, a narrow distribution of the strength data is likely beneficial much more than just increasing the strength reliability. However, a further inspection of these data reveals that all these deviations of physical properties are dependent on the material properties, and these depend on the chemical composition and process technology of the production, which are often confidential. In previous publications from this group [44,45,47], it has been demonstrated that the optimisation of the mechanical strength and a much narrower distribution of the data than that of the commercial samples are possible.

4.4. Relationship between strength and density

The strength of porous materials is dependent on the bulk density, which can be explained by the Griffith Eq. (11), where the Young's modulus has a relation with the bulk density [53]. The models proposed by many authors were tested in this work, and it was found that the relationship (6) proposed by Knudsen [53] fits the data best. The correlation of the data is illustrated by Fig. 5. The two materials are very different and their densities are in different ranges, i.e. one is easier to be pressed than the other. The large difference between the constants in the relation for the two materials indicates that the two materials are very different in the point of the sensitivity of the strength on density. This figure shows that the points are scattered around the lines with rather a long distance, which can be explained by the statistical nature of the strength data, and that even when the density and size are exactly the same for several tablets, the strength follows a distribution. Although this correlation cannot be said to be very successful, it can be concluded that these materials are in the same nature with the model proposed by Knudsen [53]. Difference between factors in the relationship obtained by the correlation implies that it is possible to optimise strength by monitoring the properties of the powder before tabletising.

5. Conclusions

Statistics reveals that the HCS data of cylindrical iron-based HTWGS catalyst scatter in rather large ranges, which is an intrinsic property inherited from the brittle fracture nature of the strength failure and the brittleness of the solid catalyst materials. It was found that the deviation range of the data can be larger than their mean value. The HCS data do not follow normal distribution, but follow a Weibull distribution, and this provides a method for the calculation of the probability of failure. Statistics of the data of the commercial catalysts shows that their mean values of the HCS data do not differ much, but the probabilities of failure at different loading conditions are rather different. One of the catalysts has a probability of failure at 10 kg/tablet as high as 18.5%, but it was proved to be useable in industry. Therefore, the probability of failure at 10 kg/tablet can be suggested as a critical value in the quality control of this catalyst.

The reason for the scattering of the strength data was investigated. The pores, defects, and discontinuations contained in catalyst tablets are comparable to the micro-cracks defined in fracture mechanics, both in the ranges of size distribution and in the performance as the origin of stress concentration. Thus the larger range of scattering of the strength data of catalysts than for other materials is reasonable, due to the high porosity and defective are expected for catalysts. However, the scattering range of the strength data is dependent on the scattering of the size and density of the tablets, which are controlled by the processing precision of the tabletising machine. Higher processing quality reduces the risk of strength failure effectively from the probabilistic point of view.

It was found that along the distribution range of the strength data, the texture properties of the tablets varied similarly. The tablets with strength in the range near lower end of the distribution have higher porosity, lower density, and higher ratio of pores in macro or

near macro range of the diameter distribution. Due to the fact that the reaction is internal diffusion controlled, this result indicates that the tablets in the range of near the high end of the distribution contribute much less than the others to the total activity of the converter. However, the tablets in the lower strength range have higher risk of strength failure. Narrow distributions of the strength, density, and size, etc. of the tablets are beneficial to industrial application.

The relationship between density and strength of the tablets can be described using a model proposed by Knudsen. The constants in the equation are sensitive to the properties of the materials. The deviation of the data from the correlation is governed by the brittle nature of the failure.

The above results demonstrate that optimisation of catalyst mechanical strength is possible through controlling and monitoring of catalyst material properties and processing parameters in catalyst manufacturing. For industrial application of fixed bed reactors using pellet catalysts, risks of mechanical strength failure could be estimated in advance through an extensive study of the probabilistic nature of the strength failure.

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