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The possibility of increasing the mechanical strength of Fe-based commercial WGS catalysts Factors analysis in the calcination process

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Abstract

The effects of various factors on the mechanical strength of iron-based high temperature water–gas shift catalyst in calcination processes has been investigated in detail by a set of second order optimum experiments. Due to one of these factors, the moisture content could not be optimized in the range examined, and the optimum values of the factors were not found by this set of experiments. Nevertheless, the experimental results and the analysis of the data give much indication on the mechanical properties of the catalyst. The calcination temperature, the heating rate, the moisture content and the calcination time respectively, all have strong effects on the resulting strength of the catalyst. The statistics of the data show that the scattering behaviour of the horizontal crushing strength of the catalyst pellet can be described by Weibull distribution. The reliability of the strength is related mainly to the value of the Weibull modulus. The results show that it is possible to reduce the probability of strength failure at low density, and that there exists much possibility to increase the reliability of strength. It has been reported that one of the samples has a Weibull modulus as high as 17.1 and a probability of failure at 10 kg/pellet as low as 6.56×10^{-13}. The value of this probability is 9 orders of magnitude lower than that of the best commercial sample at the same stress condition.

Keywords: Mechanical strength; Iron-based catalyst; Water–gas shift catalyst; Factor analysis; Calcination process

1. Introduction

The iron-based catalyst for the process of the water–gas shift (WGS) reaction is one of the catalysts being produced on a large scale in conventional chemical industry. The reaction conditions for this catalyst have often been reported to be unfavourable for the mechanical strength of catalyst. For example, the temperature rise across the reactor bed is normally high; and one of the reactants with a high partial pressure is steam, which has an unfavourable effect on the strength of most of the metal oxides. In some stages of reactor start-up and shut down, the reactor temperature can be lower than the dewpoint. There are reports of plant shut downs due to the failure of the mechanical strength of this catalyst. An unplanned catalyst replacement is extremely expensive, so that a mechanically reliable catalyst is required by the industry.

The mechanical strength of catalysts has been an important research field. The early literature

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consists of mainly one parameter experimental reports in a purpose to increase the mechanical strength of this catalyst. Gupta et al. [1] illustrated the dependence of the pellet strength on the particle size distribution of the material before pelletizing. Hogue et al. [2] reported that adding some adhesives before pelletizing can increase the strength. Putta et al. [3] added freshly precipitated $Cr(OH)_3$ and $Fe(OH)_3$ to increase the strength of the pellets.

Furen et al. [4] gave evidence that the accumulation of mechanical stress in the pellets reduces the mechanical strength. Brasoveanu et al. [5] provided experimental results on the correlation between the structural strains induced during the pelletizing and the mechanical strength of the catalyst. Based on the strength measurement of working catalysts, Hutchings proposed that the crushing strength can be used as a diagnostic test for the catalyst [6]. Recently, van den Born [7] proposed a rather complicated computing model for the simulation of the fracture strength of the catalyst carriers, however, the simulation results of this model are nearly the same as that provided by simple models from our laboratory.

Some of the results on the mechanical strength of catalyst from this group have been published elsewhere [8–11]. The measurement and the statistical method of the mechanical strength of cylindrical catalyst pellets has been discussed based on the elastic mechanics and Weibull statistics [8]. It has been proposed that the Weibull parameters of the horizontal crushing strength (HCS) and the probability of failure calculated by Weibull distribution can be used as a criterion for the comparison of the mechanical strengths [8]. A statistical relationship between the density and the strength of the catalyst has been given in another publication [9].

The factors influencing the strength in pelletizing processes were discussed in [10]. It has been shown that the precision of the pelletizing machine, the property and the treatment of the powder material and the additives, and the processing pressure of the pelletizing all have strong effects on the strength of the pellet. It has been reported that the properly manufactured pellets have a mean HCS of 103.2 kg/pellet (pellet size $\phi 9 \times 6$ mm), and that the pellets made with specially designed pelletizing equipment by the powder taken directly from an industrial production without any further treatment has a Weibull modulus of 10.1.

The basis for Weibull statistics has been discussed in some detail in previous publications [8,11]. Here again the method and the parameters are used in the comparison of the mechanical strength data. As most of the Fe-based WGS catalysts have a same size and shape, which is a cylindrical shape and a size of $\phi 9 \times 6$ mm. F_5 and F_{10}, the probability of strength failure at 5 kg/pellet and 10 kg/pellet respectively have been used in the discussion of the reliability of the catalyst.

According to Griffith's relation for the fracture strength of brittle materials, the strength is a function of the surface energy, the Young's modulus and the existing state of the microcracks inside the material [12]. In the process of calcination, the small particles from which the pellets are made up get their final physical properties, which determine the strength of the pellet. During calcination, the processing parameters such as temperature, heating rate, water content and calcination time will all have effect on the physical properties of the material, and in consequence have effect on the mechanical strength of the pellet. The goal of this work is to get some understanding on the factors and on the possibility to increase the mechanical strength of this catalyst.

2. Experimental

2.1. Samples

The original material for the calcination experiments was the powder in an industrial production process after drying, which was produced by a coprecipitation technology. It contains around 10 wt% of Cr_2O_3 and 90 wt% of Fe_2O_3 after calcination. Its DTA curve has two endothermic peaks, one is the large peak of losing water in the temperature range of lower than 100°C and the other is a small peak ending at around 320°C. The samples for comparison are the commercial pellets available in the Chinese market, some of them are made in China, some samples are imported. It is sure that these samples can represent the state of the art of the commercial products. The six commercial samples in this paper are those working in most of the WGS converters in China.

2.2. Mechanical strength measurement and data processing

The horizontal crushing strength (HCS) of the pellets were measured by MQ-200 pellet strength tester made in Dalian, China.

Combine the Weibull distribution equation [13]

$$F(\sigma) = 1 - \exp(-\beta_0 \sigma^m) \quad (1)$$

with the approximate relationship [14] in elastic mechanics

$$\sigma \approx 2P/\pi dl \quad (2)$$

thus

$$F(P) = 1 - \exp(-\beta P^m) \quad (3)$$

In these formulae σ is the maximum tensile stress in kg/cm^2 leading to fracture in the measurement of HCS, P the maximum loading in kg, $F(\sigma)$ and $F(P)$ the probability of failure at stress σ and loading P, m the Weibull modulus which characterizes the scattering behaviour of the strength data, β, β_0 are factors related to the size of the sample and the normalizing factor of stress, d is the diameter of the pellet in cm and l is the length of the catalyst pellet in cm. In this case all the pellets have a same size of $\phi 9 \times 6$ mm. In order to be consistent with industrial literature, the maximum loading P and its mean value $\bar{P}$ in kg/pellet are used in the discussion and the statistics of the mechanical strength in this paper. The Weibull parameters m and β were obtained by the regression between P and $F(P)$. The number of pellets measured for one sample depends on the scattering behaviour of the strength data. More than 70 pellets were measured for the commercial samples. 20 pellets were measured for the samples pelletized in the laboratory.

2.3. Pelletizing

After the calcination, the material was crushed to pass a sieve of 20 meshes. Then it was moved into a hermetic bottle. 1 wt% of graphite and 1 wt% of water were added and the bottle was shaken for 20 min. The material was kept in the bottle for 48 h to allow for the diffusion of the moisture. Finally the material was pelletized at a pressure of 3 $kbar/cm^2$. The filling weight was decided for the different sample by experiment to ensure that each pellet has a same size of $\phi 9 \times 6$ mm.

2.4. Calcination

2.4.1. General conditions

The original material from industry was dried for 24 h at 110°C, after that the definite amount of water according to the experimental design was added into the material. After keeping in a hermetic bottle for 48 h, 30 g of the material

Table 1
Factors and range of these factors in the experiment

Factors	T (calcination temperature, °C)	t (calcination time, h)	w (water added, wt%)	v (heating rate, °C/min)
Upper limit	500	3	8	16
Lower limit	300	1	2	2

was packed properly into a tube to form a fixed bed. The internal diameter of the tube was 25 mm. A thermocouple was fixed in the middle of the material. A flow of air at 50 ml/min was introduced from the bottom of the tube. The temperature of the material during calcination was precisely controlled.

2.4.2. Selected factors

The factors investigated and the value range of these factors are given in Table 1.

2.4.3. Experimental design

After the following linear transformation

$$\begin{cases} x_1 = (T-400)/100 \\ x_2 = t-2 \\ x_3 = (w-5)/3 \\ x_4 = (v-9)/7 \end{cases} \tag{4}$$

the four factors were transformed into normalised variables taking values between −1 and 1.

The experimental matrix is shown in Table 2. The first 15 point design matrix was taken from literature [15], two additional points, experiment 16 and 17 were added in the middle of the variable space. During the experiment, the conditions were set according to the design matrix.

2.4.4. Data treating

The Weibull parameters of the different samples were estimated from the HCS data by regression. F_5 and F_{10} were calculated by Weibull distribution. The density of the pellet was calculated from the size and the weight of the pellet, which were measured one by one precisely. For the convenience of the analysis of the effectiveness of the factors, the mean value of the HCS data were regressed by a second order equation

$$\overline{P} = b_0 x_0 + \sum_{i=1}^{N} b_i x_i + \sum_{i<j}^{N} b_{ij} x_i x_j + \sum_{i=1}^{N} b_{ii} x_i^2 \tag{5}$$

Table 2
The experimental matrix

Number	Design matrix				Real experimental condition			
	x_1	x_2	x_3	x_4	T	t	w	v
1	−1	1	−0.05	−1	300	3	4.85	2
2	−1	−1	1	1	300	1	8	16
3	−1	−1	−1	−1	300	1	2	2
4	−0.25	−0.25	−0.25	−1	375	1.75	4.25	2
5	−1	1	−1	1	300	3	2	16
6	−1	0.05	1	−0.25	300	2.05	8	8
7	1	−0.05	−1	−1	500	1.95	2	2
8	−0.6	1	1	1	340	3	8	16
9	1	−1	−1	1	500	1	2	16
10	0.05	1	−1	−0.25	405	3	2	8
11	1	−1	0.05	−0.25	500	1	5.15	8
12	1	1	1	−1	500	3	8	2
13	−0.05	−1	1	−1	395	1	8	2
14	1	−0.6	1	1	500	1.4	8	16
15	1	1	−0.6	1	500	3	3.2	16
16	0	0	0	0	400	2	5	9
17	0.5	0.5	0.5	0.5	450	2.5	6.5	12.5

Table 3
Experimental results

	Mean HCS	Density	m	β	F_5	F_{10}
1	44.5	2.350	4.84	7.12×10^{-9}	1.72×10^{-5}	4.93×10^{-4}
2	46.8	2.297	8.23	1.16×10^{-14}	6.56×10^{-9}	1.97×10^{-6}
3	44.7	2.319	8.49	6.29×10^{-15}	5.41×10^{-9}	1.94×10^{-6}
4	49.4	2.410	12.1	2.10×10^{-21}	5.93×10^{-13}	2.58×10^{-9}
5	47.5	2.315	8.29	8.08×10^{-15}	5.03×10^{-9}	1.58×10^{-6}
6	51.2	2.204	9.54	3.14×10^{-17}	1.46×10^{-10}	1.09×10^{-7}
7	42.6	2.463	10.6	3.38×10^{-18}	8.67×10^{-11}	1.35×10^{-7}
8	51.9	2.395	8.38	2.69×10^{-15}	1.94×10^{-9}	6.45×10^{-7}
9	45.4	2.444	9.24	3.13×10^{-16}	8.99×10^{-10}	5.44×10^{-7}
10	48.9	2.384	10.5	1.13×10^{-18}	2.51×10^{-11}	3.66×10^{-8}
11	40.6	2.461	10.8	2.26×10^{-18}	8.53×10^{-11}	1.56×10^{-7}
12	33.5	2.512	8.64	4.25×10^{-14}	4.65×10^{-8}	1.86×10^{-5}
13	46.7	2.423	11.3	8.95×10^{-20}	6.97×10^{-12}	1.75×10^{-8}
14	39.8	2.459	5.59	7.36×10^{-10}	5.94×10^{-6}	2.86×10^{-4}
15	37.4	2.463	5.98	2.38×10^{-10}	3.60×10^{-6}	2.27×10^{-4}
16	50.4	2.305	11.9	3.31×10^{-21}	7.11×10^{-13}	2.75×10^{-9}
17	46.5	2.330	17.9	7.71×10^{-31}	2.60×10^{-18}	6.56×10^{-13}
18	52.3	2.308	16.1	1.46×10^{-28}	2.61×10^{-17}	1.84×10^{-12}

Here x_i, x_{ij} represent the normalised factors, b_0, b_i, b_{ij}, b_{ii} the coefficients obtained by regression, $N = 4$ the number of the factors.

3. Experimental results

The experimental results are given in Table 3. The coefficients in relation (5) have been estimated as follows

$$b_0 x_0 = 50.9,\ b_i = \begin{bmatrix} -3.98 \\ -0.666 \\ -0.790 \\ 1.20 \end{bmatrix},$$

$$b_{ij} = \begin{bmatrix} -5.97 & -1.73 & -1.62 & -0.0819 \\ 0 & -2.37 & 0.916 & 0.186 \\ 0 & 0 & 1.68 & 0.0738 \\ 0 & 0 & 0 & -1.49 \end{bmatrix} \quad (6)$$

After substituting these values into relation (5), the relationship between the factors and the mean value of HCS of the samples can be obtained.

Due to $b_{33} = 1.68 > 0$, Eq. (5) does not take the maximum in the range of the factors examined. To see the correctness of this correlation, one experiment was added at the point

$$\begin{cases} x_1 = -0.343 \\ x_2 = 0.141 \\ x_3 = -0.025 \\ x_4 = 0.711 \end{cases}$$

the experimental condition is

$$\begin{cases} T = 366 \\ t = 2.14 \\ w = 4.93 \\ v = 13.98 \end{cases}$$

the results of this experiment are listed in Table 3 (sample 18). The calculated value of mean HCS according to (5) at this point is 54.0, the experimental result is 52.3, the difference between the experimental and the calculated results is rather small.

This result shows that the mean value of the HCS can be regressed by a second order equation and can be optimised by further experi-

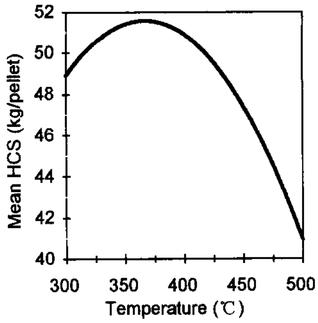

Fig. 1. Mean HCS vs. calcination temperature at $x_2 = x_3 = x_4 = 0$.

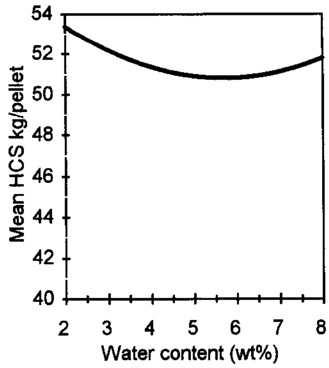

Fig. 3. Mean HCS vs. water content at $x_1 = x_2 = x_4 = 0$.

ments in the direction of the maximum gradient of the equation. The same effort trying to correlate the Weibull parameters with the experimental parameters has failed, which means that the relationship between the Weibull parameters and the experimental factors is much more complex.

4. Discussion

4.1. *Effectiveness of the factors*

Figs. 1–4 illustrate the effectiveness of the factors in the selected plane in the factor space.

These four Figures show that the calcination temperature has the strongest effect on the mean value of the strength among the four factors investigated. The curves of the mean HCS value versus calcination temperature, calcination time and heating rate have the maximum values in the range explored. On the contrary, the curve of mean HCS versus water content has a minimum in the range examined. The water content here is not really the total water amount inside the original material before calcination, it is the amount of water added after drying the material at a certain condition. The negative curvature of water content is not easy to explain, and results in the fact that no optimum point is found in the variable range examined. However, these results show that the calcination conditions have strong effects on the mechanical strength of the catalyst pellet.

The XRD patterns of the samples show that all the 18 samples have nearly same phase composition, and that the diagram change with the changing of the calcination temperature, in the way that higher calcination temperature samples get sharper peaks than lower temperature samples. The heating rate, calcination time and the water content has no obvious influence on the XRD patterns. The porosity and the pore size distribution of the samples measurements

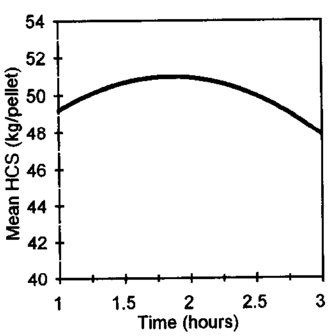

Fig. 2. Mean HCS vs. calcination time at $x_1 = x_3 = x_4 = 0$.

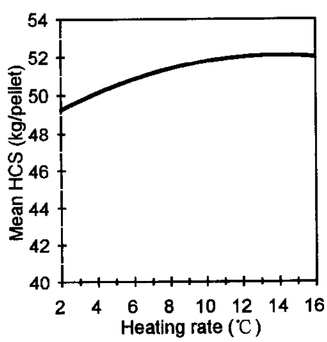

Fig. 4. Mean HCS vs. heating rate at $x_1 = x_2 = x_3 = 0$.

show that these properties have no obvious relationship with the experimental factors.

The fact that the calcination temperature has the most profound effect on the mechanical strength and on the crystallinity of the phases indicate that the surface energy and the plasticity of the small particles have a major influence on the formation of the mechanical strength. The relationship between the tensile strength of brittle materials and the physical properties has been described by the Griffith equation [12]

$$\sigma = (2E\gamma/\pi C)^{\frac{1}{2}} \quad (7)$$

in which E is the Young's modulus of the material, γ the surface energy, and C a factor characterizing the size and the state of the defects existing in the material. The typical defect size in fracture mechanics is in the range of nm–μm, which falls into the range of pore sizes in catalyst pellets. The surface energy of the small particles reduces with the increase of the crystallinity of the material and hence reduces with the increase of the calcination temperature. The experimental results show that the optimum range of calcination temperature for mechanical strength is nearly the same as that of for the activity, as experience shows that the optimum calcination temperature for activity is in the range of 350–400°C and that the high activity material has high surface energy. The Young's modulus should increase with the increase of crystallinity, while C should also increase with the increase of the crystallinity.

4.2. Statistical property of the mechanical strength

The results in Table 3 show that the probability of failure or the reliability of the mechanical strength is mainly related to the value of the Weibull modulus, as it has been shown by the comparison of the data of sample 1 and sample 12. Sample 1 has the lowest value of Weibull modulus, while sample 12 has the lowest mean value of HCS. The difference between the mean HCS of these two samples is rather large, for sample 1 the mean HCS is 44.5 kg/pellet, while for sample 12 the mean HCS is 33.5 kg/pellet. The probability of failure of sample 1 as indicated by F_5 and F_{10} is 3 and 1 orders of magnitude higher than that of sample 12, respectively.

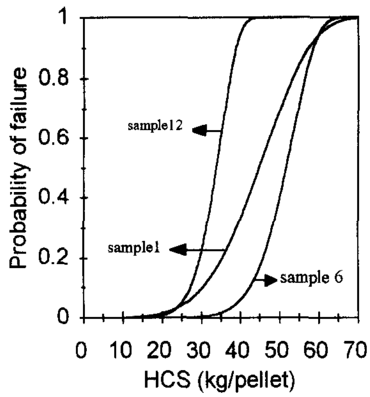

Fig. 5. The distribution curves of strength of selected samples calculated by the Weibull distribution function.

The density of the samples shows no obvious relationship with the mean value of HCS and with the Weibull parameters, as it is shown that sample 6 has the lowest density in these samples, its mean HCS and Weibull modulus are both rather high. These results show that it is possible to increase the mechanical strength at low density. Fig. 5 shows the Weibull distribution curves of the three typical samples, sample 1 has lowest Weibull modulus, sample 12 has lowest mean HCS, sample 6 has lowest density.

The results in Table 3 show that there is a great possibility in increasing the mechanical

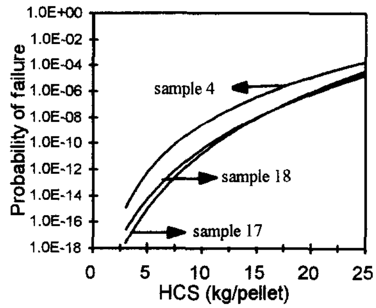

Fig. 6. The probability of failure of the three best samples in low loading range calculated by the Weibull distribution function.

Table 4
Statistical properties of currently used commercial Fe-based WGS catalysts

Catalyst	Mean HCS	Density	m	β	F_5	F_{10}
1	18.7	2.59	3.11	7.89×10^{-5}	1.17×10^{-2}	9.67×10^{-2}
2	27.8	1.91	3.59	4.75×10^{-6}	1.53×10^{-3}	1.83×10^{-2}
3	34.1	2.07	3.41	4.16×10^{-6}	1.01×10^{-3}	1.06×10^{-2}
4	36.5	missing	3.49	2.42×10^{-6}	6.65×10^{-4}	7.45×10^{-3}
5	23.3	1.94	6.23	1.96×10^{-9}	4.43×10^{-5}	3.32×10^{-3}
6	30.0	1.88	6.44	1.98×10^{-10}	6.28×10^{-6}	5.45×10^{-4}

strength and the reliability of the catalyst, as sample 17 and 18 have very high Weibull modulus and very low probability of failure. Fig. 6 illustrates the probability of strength failure of sample 17, 18 and 4 in low loading range, these samples have highest Weibull modulus. This figure shows that these samples have very low probability of failure in the loading range, in which most of the mean value of commercial samples falls. The standard in many countries for the high strength structural ceramic material for the important parts of jet engines demand the Weibull modulus of these materials to be higher than 20 [16]. The results reported here show that the mechanical properties of the porous catalyst can be made very near to that of high strength ceramics, which is calcined at high temperature and well sintered. In this set of experiment, no additives were added, no other treatment affecting the chemical properties related to catalysis introduced, and the range of the factors is in that of industrial production, the density of the pellets is also in the range of the commercial samples, therefore, it is reasonable to say that it is possible to largely increase the mechanical strength without lowering the catalytic property.

4.3. Comparison with commercial catalysts

The statistical results of the commercial samples in the same form and size of $\phi 9\times 6$ mm as currently used in industry are given in Table 4. The commercial catalysts now in operation in China with different shapes and size have also been measured. The Weibull modulus of these differently shaped catalysts are also in the range of the samples in Table 4.

The data in Table 4 show that the best commercial sample has a Weibull modulus of 6.44, while the best sample in the calcination experiment has a Weibull modulus of 17.9. The probability of failure of the best commercial sample at 10 kg/pellet is 9 orders of magnitude higher than that of sample 17 in Table 3. Fig. 7 is a comparison of the HCS data distribution curves of sample 6 in Table 4 and of sample 17 in Table 3. In the figure, the curves are the calculated values of Weibull distribution and the points are the experimental results of HCS data. This figure shows also that the scattering behaviour of HCS data can be fitted well by Weibull distribution.

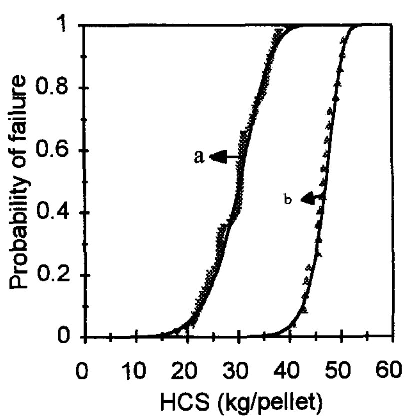

Fig. 7. Comparison of the best commercial catalyst and the sample in the experimental set with the highest Weibull distribution modulus. (a) Sample 6 in Table 4. (b) Sample 17 in Table 3.

5. Conclusions

The calcination process in the production of the catalyst is a major process for determining the mechanical properties of the catalyst. For the iron-based WGS catalyst, the processing factors in the calcination such as temperature, calcination time, heating rate and water content all have a profound effect on the resulting strength of the catalyst pellet. In the range examined, the calcination temperature is the most effective factor, and the calcination temperature, calcination time and heating rate have optimum values for the strength in the range examined. Due to that the relationship between the mean HCS and moisture content in the material takes a minimum value in the range examined, this set of experiments did not result in an optimum condition for the calcination of this catalyst. However, the results of the experiments give much understanding on the mechanical strength of the catalyst. The results reported here support the proposal that the mechanical reliability of the catalyst is mainly related to the Weibull modulus of the data. The measurement of the strength of the commercial samples show that these catalysts all have low reliability of strength. The reliability of the best sample in this set of experiments is 9 orders of magnitude higher than that of the best commercial sample. As the original material was from the industrial production process, and there are no additives except graphite and no conditions which could influence the chemical properties of the sample introduced, the catalytic property is not expected to change much. These results show it is possible to make the mechanical strength of the catalyst very reliable, and also indicate that it is possible to increase the strength at low density.

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