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A study on the surface adsorption of silver powders: The effect of technological conditions on the characterization parameters of the powder surface ☆

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Abstract

Under temperature programmed desorption conditions, the TG–DTA technique has been used to determine the adsorption capacity and the desorption activation energy of various silver powders after the powders had adsorbed ethylcellulose in a solution of ethyl acetate. Some of these silver powders had been prepared from Ag_2CO_3 or $AgNO_3$ with different reductants and dispersers, and reduction and drying treatments were at different temperatures; the others had been obtained from reduced powders by a rolling process using different rolling times.

The change pattern of relative calibrated quantity of the surface fractal on silver powders has been obtained by combining the results of TG–DTA with the adsorption capacity of nitrogen adsorbate determined by gas chromatography. The results obtained provide a direct basis for controlling various technological conditions in the production of micro-sized silver powders.

Keywords: Adsorption; Desorption kinetics; Silver powder; Surface fractal

1. Introduction

In preceding work [1], the surface morphology and the surface adsorption characteristic of micro-sized silver powders were studied by thermal analysis techniques, and we concluded that the apparent specific heat, the adsorption capacity

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and the desorption activation energy can be used to describe them. Recently some researchers [2–4] applied the concept of fractal and fractal dimensions advanced in the past few years to study some solid powder systems. In this particle system, a different surface fractal for a micro-sized powder of the same size and same material leads to different surface characteristics. Therefore the fractal can serve as a significant "mid-cosmic" characterization parameter for this type of powder system.

It can be assumed that the distribution of the adsorbate on the powder surface is mono-molecular-layered and homodispersed. Therefore the number of adsorbed molecules can be calculated from the adsorption capacity, the molecular weight and molecule size. According to the simple method of calculating the fractal [5], if the scale of measuring the powder surface is reduced by a factor n, the quantity of the measured results is N times the original one, so the value of the surface fractal can be expressed simply as

$$D = \ln N / \ln n \tag{1}$$

Two kinds of substance, whose molecules are obviously disparate in size, served as adsorbates. For the powders having different fractals, the adsorbed amount of these substances is not in the ratio of the corresponding molecular size. The adsorption capacity of the bigger molecule is assumed to be W_b, and that of smaller molecule is W_s. When the relevant parameters of the two molecules are not known exactly, the relative calibrated quantity of the surface fractal for the powder can be expressed simply as

$$D_r = A + B \ln(W_s / W_b) \tag{2}$$

where A and B are constants for two fixed adsorbates and can be defined from two characterized points in an array of determined data.

In this paper, under temperature programmed desorption (TPD) conditions, the TG–DTA technique is used to determine the adsorption capacity and the desorption activation energy of various silver powders after they have adsorbed ethylcellulose in a solution of ethyl acetate. Some of these silver powders were prepared from Ag_2CO_3 or $AgNO_3$ with different reductants and dispersers, with reducing drying at different temperatures. Others were obtained from reduced powders by a rolling process at different rolling times. In addition, we adopted the results for the adsorption capacity of nitrogen adsorbate on the same powder surface determined by gas chromatography (GC). With these two sets of adsorption data, the relative calibrated quantity of the fractal on the powder surface can be calculated by Eq. (2). Thus it is explored further that the surface morphology characteristics of prepared silver powders depend on various technological conditions.

2. Experimental

2.1. Sample preparation and pretreatment

Microfine silver powders were prepared by reduction of Ag_2CO_3 or $AgNO_3$ with different reductants and dispersers at different temperatures. One type of sample was

thus prepared after thorough washing and drying at different temperatures. Other types of sample were obtained from the powders mentioned above by a rolling process using different rolling times. Reagents and technological conditions are as follows: reductants: fatty aldehyde, organic ammonium, aromatic aldehyde, ascorbic acid, polyatomic alcohol base; dispersers: polyaromatic alcohol, aromatic alcohol ester, polyhydric alcohol, sorbitol, dihydric alcohol; reduction temperatures: 20, 27, 32, 38, 42 and 49°C; drying temperatures: 50, 80 and 130°C; rolling times: 48, 96, 144 and 192 h.

The surface of all samples was cleaned three times with ethylene glycol with a supersonic stirrer. Then the samples were immersed in ethylacetate solution containing 2.1 g l^{-1} ethylcellulose to implement adsorption treatment. The treatment was initially accompanied by supersonic stirring. Afterwards the whole system was set aside for 24 h. The completely adsorbed silver powder was then separated by a highspeed centrifuge. The treated silver powder was washed three times with analytical grade acetone to remove surplus adsorbate not truly chemically adsorbed. The silver powder was separated from the washing reagent and dried thoroughly in a desiccator at room temperature to be ready for testing.

2.2. Temperature programmed desorption (TPD)

The determinations of the adsorption capacity W_b and the desorption activation energy E were carried out in the TG–DTA part of a Rigaku Thermoflex apparatus. Experimental conditions were, heating rate 10 K min^{-1}, TG full scale 1 mg, DTA full scale ± 25 μV, chart speed 2.5 mm min^{-1}, atmosphere static air, sample mass about 20 mg, reference material α-Al_2O_3 powder, sample container, aluminium pan. An IBM personal computer was used to calculate the desorption activation energy E of various silver powders, using a set of software written by us [6].

2.3. Nitrogen adsorption and GC determination

The sample for determining specific surface area was treated by adsorbing nitrogen at the boiling temperature of liquid nitrogen. Then the adsorption capacity was determined using an SP-2305E gas chromatograph when the desorption temperature was controlled at 130°C. Finally, the specific surface area S_A of the determined sample was obtained through conversion.

3. Results and discussion

3.1. Reductants

The reductant has a decisive effect on the surface morphology of the prepared silver powders. It not only causes differences in powder size, but also creates obvious diversity on the surface fractal. The results determined for each surface parameter for these silver powders obtained by different reductants are summarized

Table 1
The effect of different reductants on the surface characterization parameters of silver powders obtained

Sample code	Reductant [a]	Specific surface area S_A/(m^2 g^{-1})	Adsorption capacity by TG W_b/%	Average size/μm	Desorption activation energy E/(kJ mol^{-1})	Relative calibrated quantity of fractal D_r
92-01	A	0.47	0.29	1.23	261	2.44
92-09	B	0.25	0.66	2.30	211	2.00
92-19	C	1.40	1.06	0.40	181	2.38
92-25	D	0.46	0.33	1.24	161	2.40
92-33	E	0.46	0.17	1.24	69	2.60

[a] A, Fatty aldehyde; B, organic ammonium; C, aromatic aldehyde; D, ascorbic acid; E, polyatomic alcohol base.

Fig. 1. The effect of different reductants on the shape of obtained silver powders.

in Table 1. It was observed using an electron microscope (see Fig. 1) that sample 92-09 (reduced by organic ammonium) had a larger particle size and a perfectly round particle shape, 92-19 (reduced by aromatic aldehyde) had a smaller particle size but its edge appeared more regular, 92-33 (reduced by polyatomic alcohol base) had a much more varied surface structure than the other samples. The electron microscope observations and the data listed in Table 1 confirm each other. In the production process, we observed that the loose density of sample 92-19 is lower than others and sample 92-33 is fiercely exothermic during reduction; these phenomena are also explained by the data listed in Table 1.

3.2. Dispersers

In the case of the same reductant fatty aldehyde, the effect of adopting different dispersers on the surface characterization parameters of the silver powders produced is summarized in Table 2. It is obvious that the effect of these dispersers on the relative calibrated quantity of the surface fractal for the silver powders obtained is much smaller than those of the reductants. Although a change of the powder size is evident, the shapes of the silver particles obtained by these dispersers do not have

Table 2
The effect of different dispersers on the surface characterization parameters of silver powders obtained

Sample code	Disperser [a]	Specific surface area S_A/(m^2 g^{-1})	Adsorption capacity by TG W_b/%	Average size/μm	Desorption activation energy E/(kJ mol^{-1})	Relative calibrated quantity of fractal D_r
92-07	a	0.42	0.44	1.38	107	2.28
92-08	b	0.47	0.49	1.23	154	2.28
92-13	c	0.48	0.40	1.19	201	2.35
92-16	d	1.73	1.37	0.33	123	2.37
92-17	e	0.44	0.41	1.29	244	2.32

[a] a, Polyaromatic alcohol; b, aromatic alcohol ester; c, polyhydric alcohol; d, sorbitol; e, dihydric alcohol.

Fig. 2. The effect of different dispersers on the shape of obtained silver powders.

obvious diversity (see Fig. 2). It is noteworthy that the rinse of sample 92-16 (dispersed by sorbitol) in the production process is more difficult, which just corresponds to the sample having the maximum D_r of the powders obtained using these dispersers.

3.3. Reduction temperatures

The effect of different reduction temperatures on the surface characteristics of the silver powders prepared by employing fatty aldehyde and polyatomic alcohol as the corresponding reductant and disperser in summarized in Table 3 and Fig. 3. It can be seen that the effect of the reduction temperature on the powder size is very obvious. The average size of silver powders obtained basically shows a decreasing trend with the increase of reduction temperature. However, the relative calibrated quantity of the surface fractal of these powders follows dissimilar behaviour. It can be imagined that there are two processes of separation and corpuscle growth of the silver atoms taking place at the same time in the reductive reaction. When reduction temperature is lower than 32°C, the main aspect of this reaction is the slow growth of separated corpuscles; when it is higher than 32°C, the quickly separated silver

Table 3
The effect of different reduction temperatures on the surface characterization parameters of silver powders obtained

Sample code	Reduction [a] temperature T/°C	Specific surface area S_A/(m^2 g^{-1})	Adsorption capacity by TG W_b/%	Average size/ μm	Desorption activation energy E/(kJ mol^{-1})	Relative calibrated quantity of fractal D_r
92-13	21	0.48	0.40	2.19	161	2.35
92-14	27	0.27	0.15	2.10	148	2.46
92-26	32	0.34	0.17	1.66	139	2.51
92-27	38	0.44	0.27	1.29	132	2.45
92-28	42	0.46	0.45	1.24	107	2.30
92-29	49	1.26	1.29	0.46	43.2	2.29

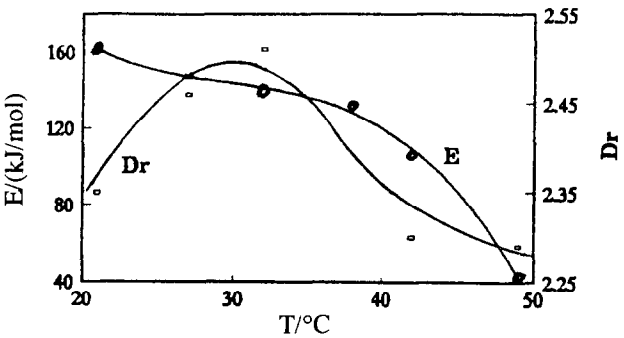

Fig. 3. Relation between E and D_r of obtained silver powder and reduction temperature T.

corpuscles group themselves into finer particles as if they "blossom" everywhere. Therefore, in order to effectively control the surface morphology and size of the silver powders, careful control of the reducing temperature is very important, in addition to choosing a suitable reductant.

Furthermore, silver powder produced at higher reduction temperature has smaller particles, so that the surface energy is higher and the surface activity is raised. This is the reason why the desorption activation energy is decreased with increase of reduction temperature.

3.4. Drying temperature

The flaky powder sample 92-19 prepared directly by a chemical method has been tested. The surface characteristics of this silver powder after drying at different temperatures are listed in Table 4. It may be seen from the listed data that the effect of drying at different temperatures on the surface characteristics of this silver powder is not large. When the drying temperature is increased progressively, a small

Table 4
The effect of drying treatment temperature on W_b and E of the thin flaky silver powder obtained by direct chemical method

Treatment temperature/ °C	Adsorption capacity by TG W_b/%	Desorption activation energy E/(kJ mol^{-1})
50	1.06	32.8
80	1.39	35.6
130	1.31	37.6

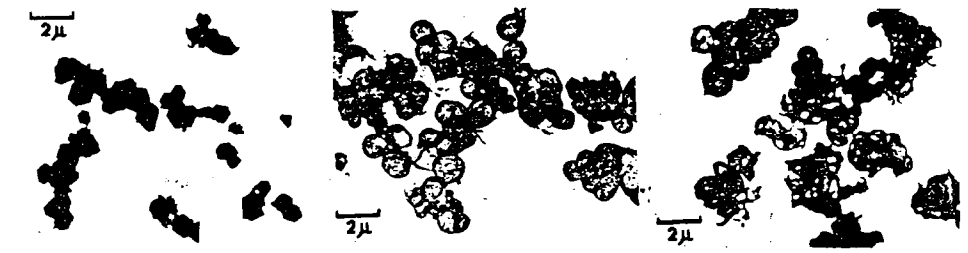

Fig. 4. The effect of different drying treatment temperatures on the shape of obtained silver powders.

increase of the adsorption capacity and the desorption activation energy can be interpreted by the "edge curl" phenomenon appearing in sample (see Fig. 4). Therefore, the drying treatment must be strictly controlled at lower temperatures in case obvious deformation occurs in the morphology of this thin flaky powder obtained by the above method.

3.5. Rolling time

After two samples (92-16 and 92-17), which have different original powder size, had been rolled for different processing times, the results showing the surface characteristics of these distinct flaky powders were summarized in Table 5 and Fig. 5. It follows that with the increase of the rolling time the adsorption capacity and the desorption activation energy display a decreasing trend. This result is evidently correlated with rolling of the silver powder so that it gradually becomes bright thin flakes. After mechanical pressing the powder (contained in the surface of the flakes) stores up suitable "cold working cumulative energy". This is the important reason that the surface activity is raised and the desorption activation energy is decreased for the silver powder produced. If the rolling time is longer, the defects, dislocation and twinning can still be observed in the high-power micrograph obtained by electron microscopy (Fig. 6).

Table 5
The effect of different rolling time on the surface characterization parameters of obtained silver powders

Sample code	Rolling Time/ h	Adsorption capacity by TG W_b/%	Desorption activation energy E/(kJ mol^{-1})	Original size of the powder/ μm
92-16	48	1.04	88.0	0.33
	96	0.75	66.6	
	144	0.78	64.9	
	192	1.03	59.2	
92-17	49	0.50	76.3	1.29
	96	0.42	75.0	
	144	0.42	74.7	
	192	1.04	72.8	

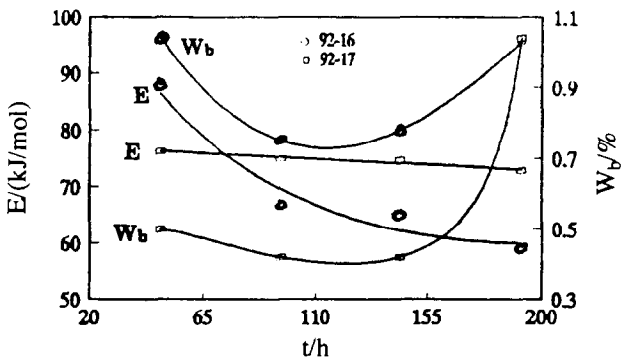

Fig. 5. Relation between E, W_b of obtained silver powder and rolling time t.

Fig. 6. The effect of different mechanical rolling time on the surface metallograph of obtained silver powders.

Certainly, if the rolling time has been increased continuously to a certain point, the adsorption capacity will suddenly increase compared with the case of shorter rolling time, perhaps because the longer rolling time causes the flaky powder to be ground further into smaller silver fragments. It is worth noting that the trend for W_b to decrease with increase of rolling time is more obviously displayed on the smaller-size powder sample. In other words, for this kind of sample it is more convenient and effective to change the surface morphology and characteristics by a mechanical process.

4. Conclusions

(1) When the surface morphology of silver powder is controlled by reproducible technological conditions, it is most important that the proper reductant is selected and the reducing temperature is carefully controlled.

(2) A high reducing temperature must be chosen so that the size of silver powder obtained is small. If we wish to obtain powder having higher fractal quantity, the selected reducing temperature ought to ensure not only enough nuclei, but also their further growth.

(3) The effect of mechanical rolling on surface morphology is more obvious for powders of small particle size than those consisting of large particles. When the rolling time is as long as about 100 h, this effect will approach a maximum.

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