

[通 讯]

Effects of Surface Monolayer Modification by Oxides on the Thermal Stability of Tin Dioxide Ultrafine Powder*

Gao Yang Zhao Biying Tang Youqi

(Institute of Physical Chemistry, Peking University, Beijing 100871)

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The gas sensors based on SnO₂ have always been in an attractive position in the field of study and application of gas sensors. The relevant researches are focused on the improvement of its sensitivity, stability and selectivity^[1]. The effects of surface modification by many oxides on the crystallite size and sensitivity of SnO₂ have been investigated by Xu *et al*^[2], and their main results can be summarized as the following: (1) The sintering of SnO₂ ultrafine powder can be retarded by surface modification to a certain extent. (2) When the SnO₂ crystallite size is controlled to be not more than 6nm, sensitivity for H₂ and CO increases steeply with decrease in its size. However, up to now there have not been any systematic and detailed reports in publication about the dispersion behavior of oxides on the surface of SnO₂ and the effects of their dispersion amounts on microstructure and properties of SnO₂ after sintered at high temperature.

In this paper, the utmost dispersion capacities of CuO, NiO, Bi₂O₃ and ZnO have been measured, and the effects of their loading on the thermal stability of SnO₂ ultrafine powder have been studied. It is observed that all of these oxides can disperse onto the surface of SnO₂ as monolayer, and their dispersion thresholds are all in good agreement with their utmost dispersion capacities estimated from a close-packed monolayer model^[3]. It is found that the thermal stability of SnO₂ ultrafine powder depends on the surface coverage of the oxides on SnO₂, and the sintering of SnO₂ grain can be effectively retarded when the monolayer coverage of the oxides are high enough.

1 Experimental

SnO₂ ultrafine powder was prepared by neutralizing a hot solution of SnCl₄ (0.5mol·L⁻¹, 90 °C) with aqueous ammonia solution (6mol·L⁻¹), followed by thorough washing with deionized

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water, drying at 100 °C for 12h and grinding. The XRD pattern showed that it is of rutile structure. Its surface area was $145\text{m}^2\cdot\text{g}^{-1}$ or $220\text{m}^2\cdot\text{g}^{-1}$ corresponding to different batches. Supported oxides, CuO, NiO, Bi_2O_3 and ZnO, were added by impregnating SnO_2 obtained with the corresponding nitrate solutions. Then the samples were dried at 90°C and calcined at 200°C for 1h and then at 500 °C for 2h. X-ray diffraction (XRD) was used to determine the phase composition, dispersion threshold and the mean size of SnO_2 crystallites. The BET surface areas of the samples were evaluated by nitrogen adsorption at -196 °C. As a comparative experiment, a few SnO_2 was sintered at 500 °C for 4h (called SnO_2^s), then was used to prepare CuO/ SnO_2^s samples. The surface area of SnO_2^s was only $28\text{m}^2\cdot\text{g}^{-1}$.

2 Results and Discussion

2.1 Monolayer dispersion of CuO, NiO, Bi_2O_3 and ZnO on the surface of SnO_2 ultrafine powder

Fig.1 gives the XRD patterns of CuO- SnO_2 samples calcined at 500 °C.

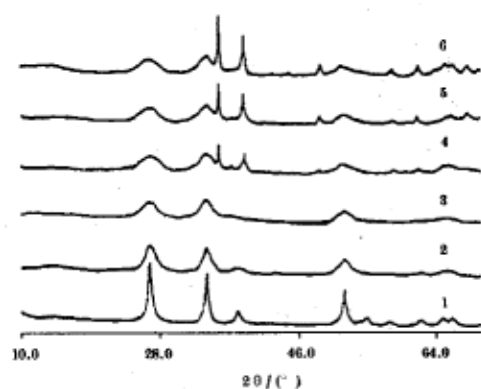


Fig.1 The XRD patterns of CuO- SnO_2 samples calcined at 500 °C for 2h

CuO content: 1) pure SnO_2 ; 2) 0.02gCuO/g SnO_2 ;
 3) 0.23gCuO/g SnO_2 ; 4) 0.42gCuO/g SnO_2 ;
 5) 0.63gCuO/g SnO_2 ; 6) 0.81gCuO/g SnO_2

It is shown in Fig.1 that only when the content of CuO in the sample is more than 0.23g CuO/g SnO_2 , do the peaks of crystalline CuO appear. Similar results can be obtained from NiO- SnO_2 , Bi_2O_3 - SnO_2 and ZnO- SnO_2 , though the contents at which the crystalline oxides can be detected are different. According to the concept that many oxides and salts can disperse spontaneously onto the surfaces of supports with highly specific surface area^[3], it is quite possible that these oxides exist on the surface of SnO_2 in monolayer state.

The dispersion threshold of CuO on the surface of SnO_2 is derived from the plot of the relative crystalline CuO content versus the total content of CuO, as shown in Fig.2. The thresholds of NiO, ZnO and Bi_2O_3 on the surface of SnO_2 are also obtained in the same way. The results are given in Table 1.

In Table 1, it can be seen that the thresholds of the four oxides on SnO_2 are all in accordance

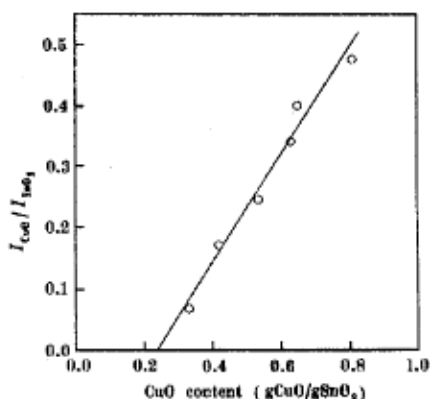


Fig.2 The relationship between the relative content of crystalline CuO and the total content of CuO in CuO- SnO_2 samples

with their utmost monolayer capacities estimated from the simple close-packed monolayer model^[3]. But it should be pointed out that the SnO₂ as the support was only heated at 100 °C, so its surface area would change after supporting the oxide and calcining again. In addition, this change would depend on the content of supported oxide. However, the surface areas that could be determined are only those of the samples calcined at 500 °C, not that of SnO₂. We consider that the utmost dispersion capacities on 100m² SnO₂ calculated from the original surface area of SnO₂ seem to be workable. The reason is that there is little increase in the crystallite size of SnO₂ in the samples if the content of supported oxide is greater than its threshold (see Fig.4). In order to confirm this point, the threshold of CuO/SnO₂ sample is determined (shown as Fig.3 and Table 1). The result agrees with that of CuO-SnO₂, and the threshold is also in accordance with the utmost capacity estimated from a close-packed monolayer model.

Table 1 The dispersion thresholds of oxides on the surface of SnO₂

Oxides	Original surface area of SnO ₂ (m ² ·g ⁻¹)	Experimental value		Calculation value
		(g/g SnO ₂)	(g/100m ²)	(g/100m ²)
CuO	145	0.24	0.17	0.19
NiO	145	0.25	0.17	0.18
Bi ₂ O ₃	145	0.54	0.37	0.38
ZnO	220	0.45	0.20	0.20
CuO*	28	0.05	0.18	0.19

* SnO₂ in the sample had been calcined at 500 °C for 4h in advance.

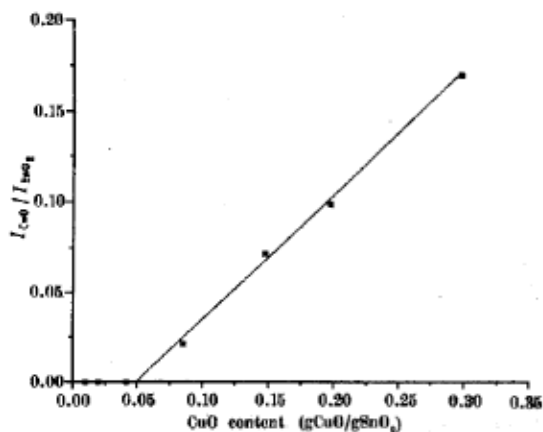


Fig.3 The relationship between the relative content of crystalline CuO and the total content of CuO in CuO/SnO₂ samples

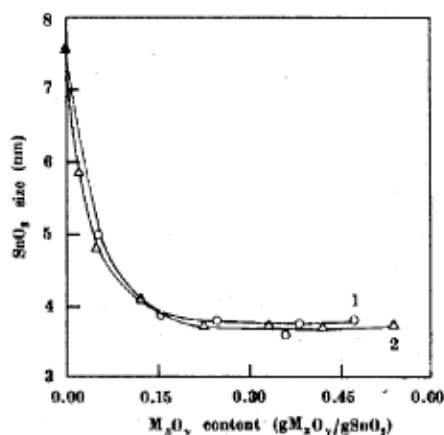


Fig.4 The relationship between the mean size of crystalline SnO₂ and the total amount of supported oxides
1) NiO-SnO₂ ; 2) CuO-SnO₂

SnO₂ is of rutile structure and its dominant exposing crystal face is (110)^[4], therefore, there are not any so called "surface vacant sites" available to contain cations on its surface. Obviously, the above-mentioned results can hardly be understood according to the incorporation model reported recently^[5]. It is apparent that the results are very valuable for constructing a more satisfactory structure model of monolayer dispersion state.

2.2 The relationship between the thermal stability of SnO₂ ultrafine powder and the amount of dispersed oxide on SnO₂ surface

The mean size of SnO₂ crystallites is evaluated from the width of XRD peak of the face(110) on the basis of scherrer's equation. The thermal stability of pure SnO₂ ultrafine powder is very poor. The crystallite size of SnO₂ increases obviously with the increase in the calcination temperature (3.1nm, 4.1nm, 5.4nm and 7.6nm for 100 °C, 300 °C, 400 °C and 500 °C, respectively). The relationships between the sizes of crystalline SnO₂ and the total contents of supported oxide in CuO-SnO₂ and NiO-SnO₂ samples sintered at 500 °C are shown in Fig.4. It can be concluded that the size of SnO₂ crystallites decreases with the increasing of the content of the supported oxide, and the sintering of SnO₂ ultrafine powder can be suppressed to a greater extent. When the content of oxide approaches to its monolayer dispersion threshold, the minimum SnO₂ crystallites can be obtained. If the loading is above the threshold, SnO₂ crystallite size will not change any more. The results obtained from ZnO-SnO₂ and Bi₂O₃-SnO₂ are similar to that of CuO-SnO₂.

In short, there is a good correlation between the thermal stability of SnO₂ ultrafine powder and the dispersion amount of the oxide on SnO₂ in monolayer state. The results of BET surface areas of these samples indicate a similar rule. Whether there is a corresponding relation between the sensitivity of SnO₂ ultrafine powder and the content of the dispersed oxide is still under study now.

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氧化物表面单层改性对 SnO₂ 超微粒子热稳定性的影响

高 扬 赵壁英 唐有祺

(北京大学物理化学研究所, 北京 100871)

摘 要 研究了氧化物在气敏材料二氧化锡超细粉表面的分散行为及分散量对二氧化锡热稳定性的影响. 结果表明, 氧化铜、氧化镍、氧化铋和氧化锌在二氧化锡表面均能单层分散; 分散阈值均与按密置单层模型计算的最大分散容量相符, 负载二氧化锡的表面覆盖度与其热稳定性之间有很好的对应关系; 单层覆盖率达到一定程度二氧化锡高温烧结便可基本得到抑制.

关键词: SnO₂ 超细粉, 单层分散, 热稳定性, SnO₂ 气敏材料.