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Monolayer dispersion of oxide additives on SnO_2 and their promoting effects on thermal stability of SnO_2 ultrafine particles

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The dispersion behavior of some oxides on the surface of SnO_2 and the effects on the thermal stability of SnO_2 have been studied. The results show that many oxides such as NiO, CuO, ZnO, Bi_2O_3, MoO_3, Cr_2O_3 and Sb_2O_3 can disperse onto the surface of SnO_2 by impregnation method or dry method—mixing a compound with the support thoroughly, followed by calcination at an appropriate temperature. The utmost dispersion capacities of these oxides on the surface of SnO_2 are measured and they are all in good agreement with those estimated by a close-packed monolayer model. These oxides dispersed on the surface of SnO_2 can retard the decrease in the specific surface areas of the samples and the increase in the crystallite size of SnO_2 during calcination. In numerous effect factors, the surface coverage is a key factor. It is easy to stabilize the size of SnO_2 grains to be 6 nm by this means, and the higher the valence of the cation of oxide, the stronger the stabilizing effects.

1. Introduction

Gas sensors based on SnO_2 have always been in a dominant position in the field of the study and application. Although this kind of sensors has been put in application successfully, there are still many problems remaining to be solved, such as making further improvement on stability, sensibility and selectivity [1, 2]. Contrary to the success in applications, the gas-sensing mechanism of SnO_2 is still obscure. Many factors, such as the microstructure of the polycrystalline SnO_2, surface adsorption, the reaction on the interface as well as the states and effectiveness of the additive, can all affect the sensing properties of semiconductor gas sensors. Therefore, it is difficult to use a uniform model to completely elucidate the nature of the gas sensitivity and the effects of additives [3, 4]. In the other hand, with the development of some new reactions, SnO_2 has shown some special properties as an active component or as a support in some catalytic process [5].

It is relatively easy to prepare SnO_2 ultrafine powder, which is a favorable factor for its application in catalysis and gas sensors. However, due to the poor thermal stability of the pure ultrafine powder [6], its application is confined to a great extent. Therefore, it is very meaningful to improve the thermal stability of SnO_2 ultrafine powder. Since it was reported that a small amount of additives can improve the gas-sensing nature greatly, a lot of metal or non-metal oxides have been used in manufacturing gas sensors with different characteristics [1]. According to the literature, the functions of additives can be classified into three ways:

1. Controlling the size of crystallite SnO_2 grains [7]
2. Catalysis [8]
3. Changing the electronic structure of SnO_2 [9]

It has been proved that many additives are quite effective to stabilize the crystalline SnO_2 during calcination as well as the sensing operation at high temperature, and when the size of SnO_2 grains is controlled at smaller than 6 nm, the gas-senoring sensitivity will be improved greatly [10]. Xu etc. reported the states of many additive oxides with content of 5% in atomic composition on the surface of SnO_2 and the effects on the microstructure as well as electricity performance [11]. They considered that most additives are well dispersed on the surface of SnO_2 and play an important role in improving the thermal stability of SnO_2 ultrafine powder. However, the relationship between the amounts of oxides as additives and the thermal stability of SnO_2 has not been reported systematically.

Xie and Tang *et al.* of our lab proposed a principle of spontaneous monolayer dispersion of oxides and salts onto surfaces of supports [12]. This theory suggests that a great many oxides and salts can disperse spontaneously onto the surfaces of supports to form a monolayer or submonolayer, because in these cases the monolayer is a thermodynamically stable form. The utmost dispersion capacity is called dispersion threshold. Only when the amount of a kind of oxide or salt exceeds its threshold on a support, the surplus oxide or salt exists as a separate crystalline state or amorphous phase. Oxides or salts in a monolayer state and in their crystalline

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or amorphous state behave differently in many respects, which have been proved by the detection of X-ray diffraction (XRD), temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), laser Raman spectroscopy (LRS), thermogravimetric analysis (TGA) and differential thermal analysis (DTA). There have been large quantities of reports about the phenomena of monolayer dispersion as well as the thresholds of oxides [13], but these reports mainly focus on the supports such as Al_2O_3, TiO_2, ZrO_2, SiO_2 and CeO_2 [14]. The aim of the present paper is to study the dispersion of a large number of oxides on the surface of SnO_2, to measure dispersion thresholds of these oxides on SnO_2 and find out the relationship between the amount of the oxide additives and the thermal stability of SnO_2 particles. We reported that the thermal stability of TiO_2 or ZrO_2 can be improved greatly by dispersing a layer of active component onto its surface before calcination at high temperature [15]. By using this method, a series TiO_2 or ZrO_2-supported catalysts with highly specific surface area have been prepared. In this work on SnO_2-supported oxides, it is proved again that this method is common and effective for preparation catalysts with highly specific surface area.

2. Experimental procedure

2.1. Sample preparation

The precipitation method was used to prepare SnO_2 ultrafine powder. A solution of $SnCl_4$ (0.5 $mol \cdot L^{-1}$) was kept at 9°C in water bath. Aqueous ammonia solution (6 $mol \cdot L^{-1}$) was dripped slowly into the $SnCl_4$ solution until the pH value reached 7, and followed by washing with deionized water till the Cl^{-1} could not be detected by $AgNO_3$ solution. The precipitation was dried at 100°C for 15 h and grinded. There were some small differences in specific surfaces and crystallite sizes for the SnO_2 powders prepared in different batches.

The samples of CuO/SnO_2, ZnO/SnO_2, NiO/SnO_2, Cr_2O_3/SnO_2 and Bi_2O_3/SnO_2 were prepared as following. The nitrate of the selected metal with calculated amount was dissolved in water. The samples were obtained by impregnating SnO_2 powder with three nitrate solutions followed by drying and calcining. The calcination procedure was heating at 200°C for 2 h, cooling, grinding, and then calcining at 500°C for 4 h. The sample of MoO_3/SnO_2 was prepared by impregnation with $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ solution. To compare with the impregnation method and prove the spontaneity of the dispersion process, we used a dry method (mixing the oxides and salts with SnO_2 thoroughly and calcining at an appropriate temperature) to prepare the samples of MoO_3/SnO_2 and Sb_2O_3/SnO_2.

2.2. The physicochemical measurements

2.2.1. X-ray diffraction

XRD patterns were obtained on BD-86 X-ray diffractometer operated at 40 kV and 20 mA, with Cu K_α radiation and Ni filter. The scanning speed for phase identification was 8°/min and that for XRD quantitative phase analysis was 1.2°/min. The peak intensity ratio between one of the diffraction peaks of the supported oxide and SnO_2 (110) was used to represent the relative crystalline content of supported oxide in a sample. Then, a straightline of the residual crystalline content of supported oxide versus its total content was obtained. The straight line gave an intercept corresponding to the utmost dispersion capacity—the dispersion threshold [16]. The mean crystallite size of SnO_2 was evaluated from the broadening of the peak of SnO_2 (110) based on Scherrer equation after necessary correction.

2.2.2. X-Ray photoelectron spectroscopy

In order to compare with the results derived from XRD, a surface-sensitive technique, XPS was used to characterize the sample of CuO/SnO_2. The XPS experiment was carried out in VG-ESCA-LAB-5 electron spectrometer using Al k_α radiation (40 kV, 10 mA). The spectra were obtained at room temperature and 10^{-8} Torr. The XPS peak intensity ratios of $I_{Cu2P3/2}/I_{Sn3d5/2}$ were taken as the measurement of the relative concentration of CuO on the surface of SnO_2. The dispersion threshold of CuO on the surface of SnO_2 was obtained by the CuO content corresponding to the turning point in the curve of $I_{Cu2P3/2}/I_{Sn3d5/2}$ versus the CuO content in CuO/SnO_2 sample [17].

2.2.3. Specific surface area (SA)

SA was evaluated from nitrogen adsorption data measured at −196°C using the Brunaner Emmett Teller (BET) method.

3. Results and discussion

XRD result shows that the nanoscale SnO_2 heated at 100°C for 1 h is of rutile structure with the low crystallinity, which is corresponding to the results reported [17]. The SA of SnO_2 can be as large as 220 m^2/g after heating at 100°C, but it rapidly decreases to 131 m^2/g and 30 m^2/g after calcination at 300 and 500°C, respectively. Relatively, the mean crystallite size of SnO_2 is 3.1 nm after heating at 100°C, and it tremendously increases to 4.1 nm and 7.6 nm after calcination at 300 and 500°C, respectively. Thus, it is clear that the thermal stability of pure nanoscale SnO_2 is very poor, which is agreement with the results reported in literature [11, 18].

3.1. Spontaneously monolayer dispersion of oxides on the surface of SnO_2 and the measurements of their dispersion thresholds

Fig. 1 shows the XRD results of CuO/SnO_2 samples obtained by impregnation and calcination at 500°C.

Only the peaks of SnO_2 are detected in CuO/SnO_2 samples with the low content of CuO. The peaks of crystalline CuO appear when the content of CuO exceeds 0.23 g CuO/g SnO_2. However, no new phase is detected by XRD even if CuO content is very high. According

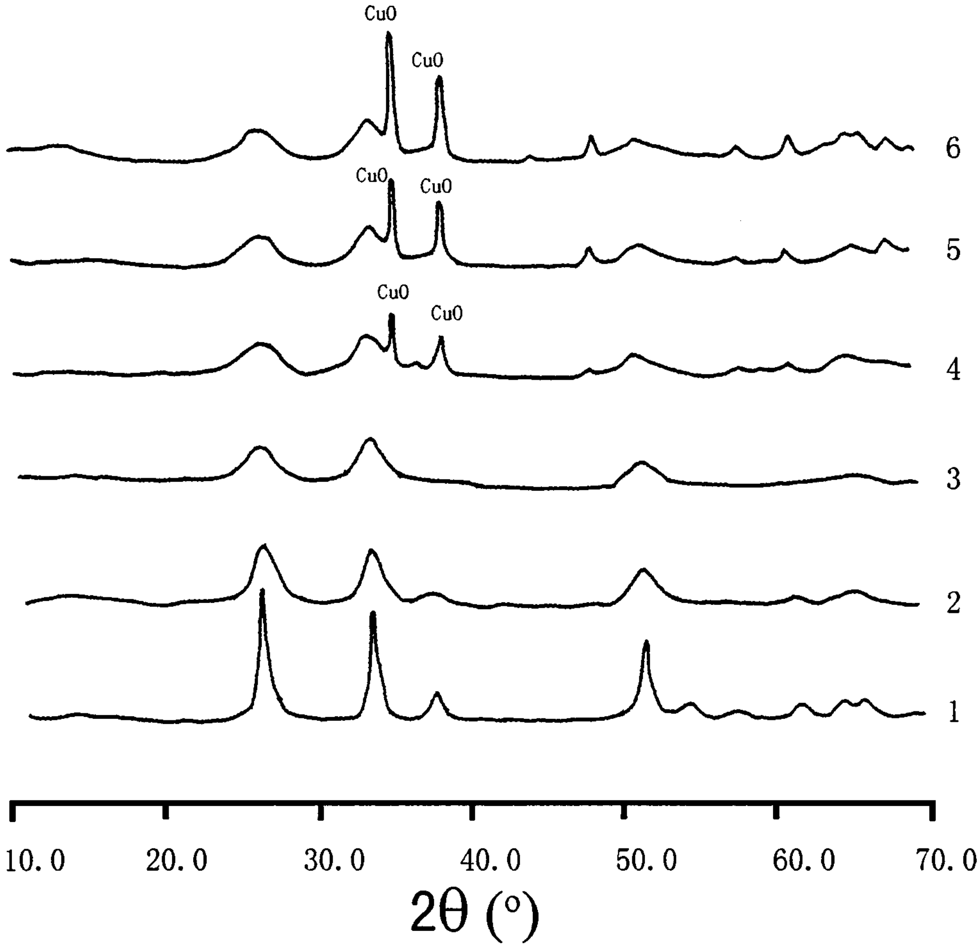

Figure 1 XRD patterns of pure SnO_2 and CuO/SnO_2 after calcination at 500°C. 1. Pure SnO_2 2. 0.02 g CuO/SnO_2 3. 0.23 g CuO/SnO_2 4. 0.42 g CuO/SnO_2 5. 0.53 g CuO/SnO_2 6. 0.81 g CuO/SnO_2.

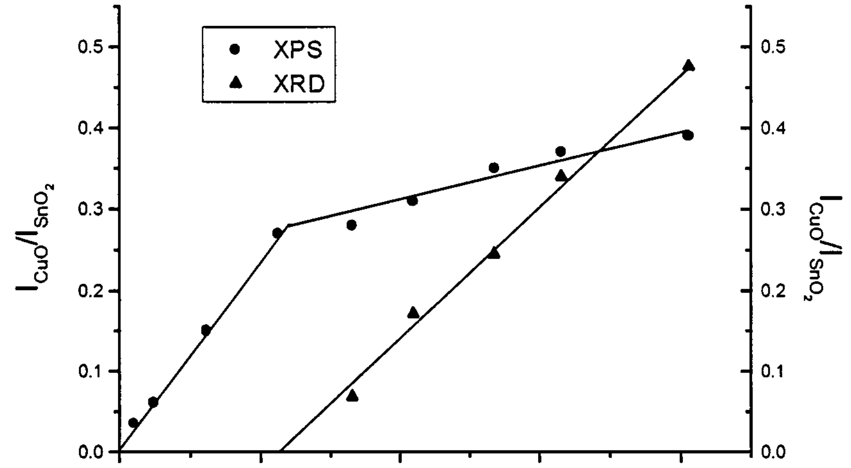

Figure 2 XRD and XPS quantitative results of CuO/SnO_2 calcined at 500°C.

to the principle of spontaneous monolayer dispersion of oxides and salts onto surfaces of supports, we think that CuO may disperse on the surface of SnO_2 as a monolayer and have a certain dispersion threshold. In other samples prepared by impregnation or dry method, we observed the similar phenomena as CuO/SnO_2, but the contents of oxides at which peaks of crystalline oxide turn out are different. Thus, these oxides may also disperse on the surface of SnO_2 as a monolayer.

Fig. 2 shows the dispersion threshold of CuO in the system of CuO/SnO_2, which is measured by XRD and XPS quantitative phase analysis, respectively.

Since XPS is a surface sensitive technique, an oxide monolayer-dispersed on the surface of a support will give an XPS signal much stronger than that given by the crystalline oxide. From Fig. 2, one can see that with low CuO content, the intensity ratios I_{Cu}/I_{Sn} as a function of the total content of CuO rapidly grow with the

TABLE I The dispersion thresholds of oxides on the surface of SnO_2

Supported compounds	The initial SA of SnO_2 (m^2g^{-1})	Dispersion threshold (Experimental value) ($g/g\ SnO_2$)	Dispersion threshold (Experimental value) ($g/100\ m^2$)	Dispersion threshold based on a closed-packed monolayer model [12] ($g/100\ m^2$)	Methods used
ZnO	225	0.45	0.20	0.20	XRD
CuO	145	0.24	0.19	0.19	XRD XPS
CuO[a]	28	0.05	0.19	0.19	XRD
NiO	145	0.25	0.18	0.18	XRD
Bi_2O_3	145	0.54	0.38	0.38	XRD
MoO_3	198	0.21	0.12	0.12	XRD
MoO_3[b]	70	0.08	0.12	0.12	XRD
Cr_2O_3	198	0.21	0.14	0.14	XRD
Sb_2O_3[c]	70	0.11	0.19	0.19	XRD

[a] SnO_2 as the support has been calcined at 500°C before impregnation;
[b] MoO_3/SnO_2 is prepared by dry method;
[c] Sb_2O_3/SnO_2 is prepared by dry method and calcined at 400°C. The residual crystalline oxide exists as Sb_2O_4 and the dispersion threshold is estimated on the basis of Sb^{4+}.

increase in the content of CuO, which shows that CuO exists on the surface of SnO_2. With the increase in the content of CuO, a turning point in the curve of I_{Cu}/I_{Sn} versus the content of CuO turns out, which suggests that when CuO content exceeds a certain value, the surplus CuO exists as CuO crystallite. The turning point of the curve corresponds to the utmost dispersion capacity, which is 0.24 g CuO/g SnO_2 and in good agreement with the dispersion threshold obtained by XRD. The results above strongly support our viewpoint that CuO has dispersed on the surface of SnO_2 to form a monolayer, and possesses a certain dispersion threshold.

We measure all samples by XRD, including NiO/SnO_2, ZnO/SnO_2, Bi_2O_3/SnO_2, Cr_2O_3/SnO_2 and MoO_3/SnO_2 obtained by the impregnation method and MoO_3/SnO_2 and Sb_2O_3/SnO_2 prepared by dry method. The results show that they all display similar trend as the system of CuO/SnO_2. Table I gives the dispersion thresholds of these oxides on the surface of SnO_2.

The experimental dispersion thresholds of the oxides listed in Table I are all in good agreement with the utmost dispersion capacities evaluated according to a close-packed monolayer model, which is a very interesting phenomena and worth probing deeply. It was reported that most oxides and salts can spontaneously disperse on the surfaces of supports, such as γ-Al_2O_3, TiO_2, active carbon, ZrO_2 and CeO_2 to form submonolayers instead of monolayers. In other words, the dispersion thresholds of most oxides on the supports above are lower than those estimated on the basis of a close-packed monolayer model. However, to our surprise, all of the oxides studied can disperse on the surface of SnO_2 to form a quite complete monolayer. This result will be helpful for us to prepare monolayer-dispersed systems and to probe into the mechanism of monolayer dispersion and structural model of dispersion state.

It should be pointed out that we use the SA of SnO_2 before impregnation to calculate the dispersion thresholds of these oxides. The reasons are the followings:

First, although the samples are calcined at 500°C after impregnation, the crystallite size of SnO_2 as support changes only a little in comparison with that before impregnation. For example, the crystallite size of SnO_2 only dried at 100°C is 3.1 nm, while the mean crystallite size of SnO_2 in these samples calcined at 500°C can be kept at between 3.5 and 3.7 nm as the contents of the dispersed oxides are near their thresholds. Second, since it is impossible to measure the true SA of SnO_2 covered by the oxides as additives, and it is doubtable to derive the SA of SnO_2 in a sample only by weight calibration. Finally, from Table I, we can see that the dispersion threshold of CuO on the surface of SnO_2 with the initial SA 145 m^2/g is in good agreement with the value estimated, and the same thing happens when the SnO_2 with the initial SA 28 m^2/g is adopted. Similarly, the dispersion thresholds of MoO_3 dispersed on the surface of SnO_2 with different SA are also the same. These results prove that it is quite reasonable and feasible to use the initial SA of SnO_2 to calculate the dispersion threshold.

3.2. Effects of surface monolayer modification with oxides on the thermal stability of tin dioxide ultrafine powder

3.2.1. *The effect on size of crystalline SnO_2*

The relationships between the sizes of crystalline SnO_2 and the total contents of supported oxides in NiO/SnO_2 and CuO/ SnO_2 samples after calcination at 500°C are shown in Fig. 3.

We can see that when the amount of NiO or CuO is low, the crystallite size of SnO_2 decreases with the increase in the content of the supported oxide very quickly. When the content of oxide approaches to half of its threshold (0.12 g NiO/SnO_2 or 0.12 g CuO/SnO_2), the increase in the size of crystalline SnO_2 is suppressed to a great extent. As the content of oxide reaches or surpasses the threshold, SnO_2 crystallite size reaches a minimum value and does not change any more. It can be concluded from the result above that there is a good corresponding correlation between the size of crystalline SnO_2 in the sample and the surface coverage of the oxide on SnO_2. This phenomenon can be termed as threshold effect. It should be emphasized that the monolayer dispersion of NiO or CuO on the surface of SnO_2 is quite effective to suppress the sintering between crystalline SnO_2 grains and the growing of crystalline

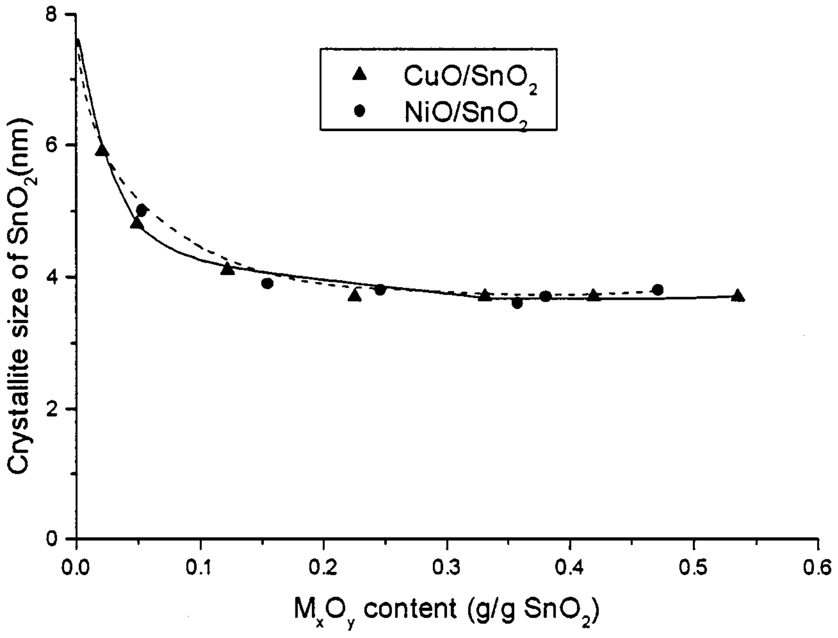

Figure 3 The relationship between the mean size of crystalline SnO_2 and the total content of supported oxide in NiO/SnO_2 and CuO/SnO_2 samples calcinated at 500°C.

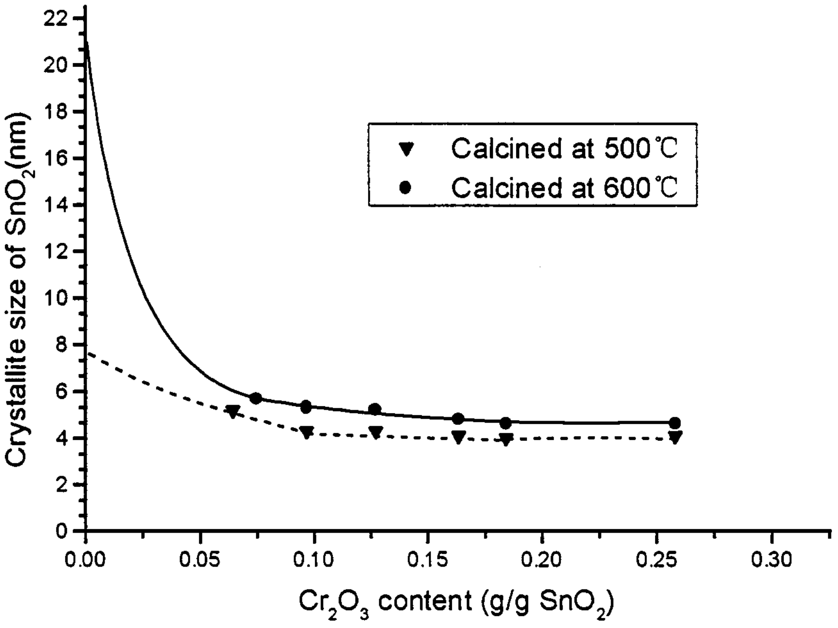

Figure 4 The mean crystallite size of SnO_2 versus the total content of Cr_2O_3 in Cr_2O_3/SnO_2 calcined at 500°C and 600°C.

SnO_2 grains. After calcination at 500°C, the crystalline size of pure SnO_2 increases to 7.6 nm, while that of SnO_2 in the sample with NiO or CuO content corresponding to the utmost dispersion capacity still remains at about 3.7 nm. This size is close but a little bit larger than that of the pure SnO_2 only dried at 100°C. The results for ZnO/SnO_2, Bi_2O_3/SnO_2, Cr_2O_3/SnO_2 and MoO_3/SnO_2 prepared by impregnation are similar to that of CuO/SnO_2 or NiO/SnO_2. Moreover, the crystalline size of SnO_2 in the sample of Cr_2O_3/SnO_2 or MoO_3/SnO_2 can still be kept at less than 5 nm even after calcination at 600°C, as shown in Figs 4–5.

Thus, we can conclude that the monolayer modification of oxide is very effective to suppress the growth and sintering of SnO_2 ultrafine particles during the calcination at high temperature and there is a threshold effect in the relationship between the size of crystalline SnO_2 and the content of the oxide as additive.

For ZrO_2 support, the similar phenomenon has been reported many times [15, 19, 20]. Our research group did a systematic research on this phenomenon and found that it is very widespread for the supports such as ZrO_2 and TiO_2 [15, 19]. The reason is that both of the sintering between particles and the grain growth proceed through a surface diffusion mechanism. So, it can be expected that if we disperse some oxides on the surface of SnO_2 as the size of SnO_2 grains is quite small and then calcine the samples at a high temperature, the growth of SnO_2 grains and the sintering between SnO_2 grains can be retarded and the thermal stability of the texture can be improved to a great extent. It can also be expected that when the content of the additive

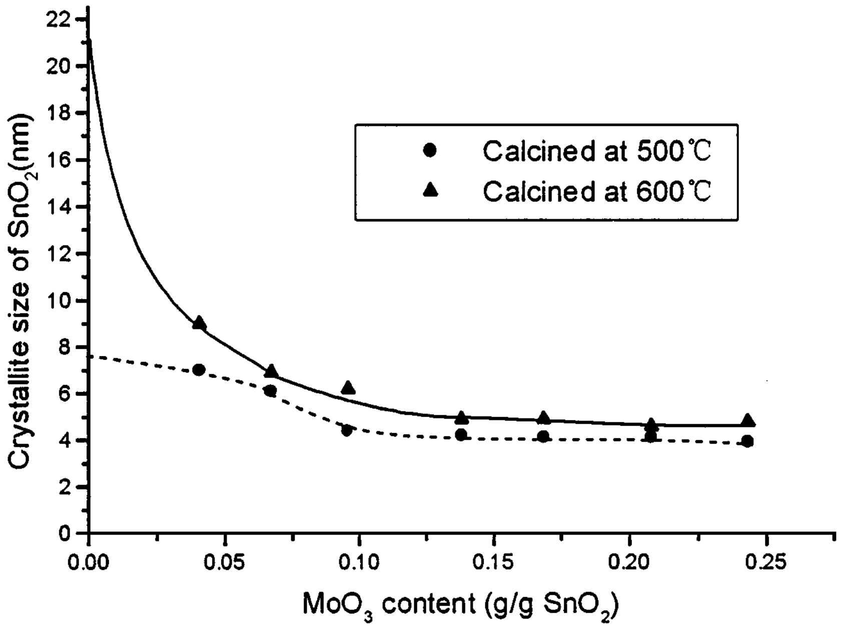

Figure 5 The mean crystallite size of SnO_2 versus the total content of MoO_3 in MoO_3/SnO_2 calcined at 500°C and 600°C.

approaches to its monolayer dispersion threshold, the utmost surface coverage on SnO_2 will be reached, and the best thermal stability of SnO_2 will be obtained. The experimental results for a series of samples based on the support of SnO_2 are exactly the case.

It is noted that the oxides with different cationic valence such as CuO, Cr_2O_3 and MoO_3 exhibit different effects against the sintering of SnO_2. By taking mol M/g SnO_2 as the accounting unit, where M stands for metal cation in oxides, the stabilizing effects against the sintering of SnO_2 rank as the following: $MoO_3 > Cr_2O_3 > CuO$, which is just contrary to their ranks in stoichiometric proportion (M: O): $MoO_3 < Cr_2O_3 < CuO$. The same trend also exhibits in other samples. This trend can be explained reasonably with the viewpoint of monolayer dispersion. In the case of the samples with same mole content of oxide additive, the higher the valence of the cations in oxides, the more O^{2-} coordinating with one cation and the larger surface of SnO_2 covered, therefore the better the stabilizing effects against the sintering of SnO_2. In another word, when these dispersed oxides form a complete monolayer on the surface of SnO_2, the amounts of the oxides needed are different: the mole ratios of MoO_3, Cr_2O_3, CuO are 1 : 2 : 3. Xu *et al.* investigated the effects of oxides containing different metal elements against the sintering of SnO_2 [7]. The contents of M were fixed at 5% in the atomic composition defined as M/(M+Sn). It can also be seen from their data reported that the higher the valence of the cation, the more effective the oxide to stabilize the SnO_2 particles. In addition, they reported that the stabilizing effects of the alkaline

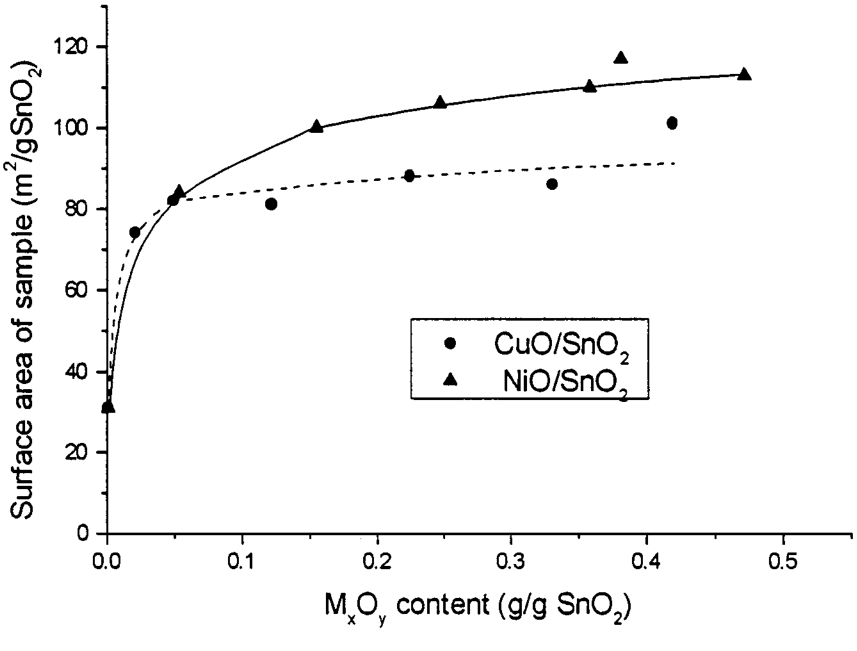

Figure 6 The specific surface areas of SnO_2 in CuO/SnO_2 and NiO/SnO_2 calcined at 500°C versus the total content of supported oxides.

oxides or alkaline earth oxides against the sintering of SnO_2 enhanced with the increase in cationic radius. According to the viewpoint of monolayer dispersion, their results can be explained as the following: the bigger the cationic radius of the oxide, the more O^{2-} coordinating with one cation, and the larger surface of SnO_2 occupied.

3.2.2. Effects on the specific surface areas of the samples

The experimental results show that surface monolayer modification can greatly improve the resistance of SnO_2 to the thermal sintering and stabilize the SA of SnO_2 in the samples. Fig. 6 shows the relationship between the SA of SnO_2 and the total content of CuO and NiO in the samples after calcination at 500°C.

Obviously, when the loading of the oxide is low, the SA of SnO_2 in the sample goes up with the increase in the content of the oxide. And when the content of oxide reaches and surpasses the dispersion threshold, the SA of SnO_2 in the sample comes up to a maximum value and dose not change any more. The results of other samples present a similar trend. This phenomenon is in good agreement with the relationship between the mean crystallite size of SnO_2 and the total content of oxide additive in the sample calcined at 500°C, and the reasons behind these phenomena are same. However, since the gathering of particles and other factors can also affect the SA, the data of SA are not as regular as those of the crystallite size of SnO_2.

In addition, we observe that the higher the cationic valence of supported oxides, the stronger the effects against the decrease in the SA of SnO_2. Xu *et al.* also reported the similar phenomena for some samples [11].

4. Conclusions

1. A lot of oxides such as NiO, CuO, ZnO, Bi_2O_3, MoO_3, Cr_2O_3, Sb_2O_3 and so on can disperse on the surface of SnO_2 to form a quite complete monolayer and the dispersion thresholds are all close to upper limit values of dispersion capacities estimated according to a close-packed monolayer model.

2. The monolayer dispersions of these oxides on the surface of the SnO_2 ultrafine powder can retard the decrease in the specific surface area of SnO_2 and the increase in the crystallite size of SnO_2 during the calcination at high temperature. The higher the cationic valence of the oxides, the stronger the stabilizing effects.

3. For each series of samples studied, there is a good corresponding relationship between the specific surface area of the sample or the crystallite size of SnO_2 and the surface coverage of the oxide additive on SnO_2 at a high temperature.

4. By this means, it is easy to stabilize the crystalline size of SnO_2 at 6 nm or less.

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